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THE DIRECT DETERMINATION OF THE EXCESS ENTHALPY
OF GASEOUS MIXTURES UNDER PRESSURE

BY



JONG IL LEE

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES IN
PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE IN
CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled "THE DIRECT DETERMINATION OF THE EXCESS ENTHALPY OF GASEOUS MIXTURES UNDER PRESSURE" submitted by Jong Il Lee in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering.

ABSTRACT

A flow-type isothermal calorimeter was designed, constructed, and tested to directly measure the excess enthalpy of binary gaseous mixtures.

The calorimeter was tested with hydrogen-nitrogen mixtures at temperatures of 20, 7, -3, and -73°C and for the pressure range of up to 130 atm. The experimental data are in good agreement with the literature to within the experimental uncertainty, 5 percent.

The experiment was performed for the nitrogen-carbon dioxide system at 40°C and for the pressures up to 130 atm. The excess enthalpy data of this system are compared with values predicted using the B-W-R equation of state, the virial equation of state, the generalized method, and the liquid theories.

The behavior of the excess enthalpy as a function of density obeys binary collision theory in the region of low densities. In the neighbourhood of the critical point of one component of the mixture, the excess enthalpy follows the behavior of the enthalpy of this component.

ABSTRACT

A flow-type isothermal calorimeter was designed, constructed, and tested to directly measure the excess enthalpy of binary gaseous mixtures.

The calorimeter was tested with hydrogen-nitrogen mixtures at temperatures of 20, 5, -3, and -73°C and for the pressure range of up to 150 atm. The experimental

data are in good agreement with the literature to within the experimental uncertainty, 5 percent.

The experiment was performed for the purpose of obtaining data for the pressure range of up to 150 atm. The experimental data are in good agreement with the literature to within the experimental uncertainty, 5 percent.

The behavior of the excess enthalpy as a function of density obeys binary collision theory in the region of low densities. In the neighborhood of the critical point of one component of the mixture, the excess enthalpy follows the behavior of the enthalpy of this component.

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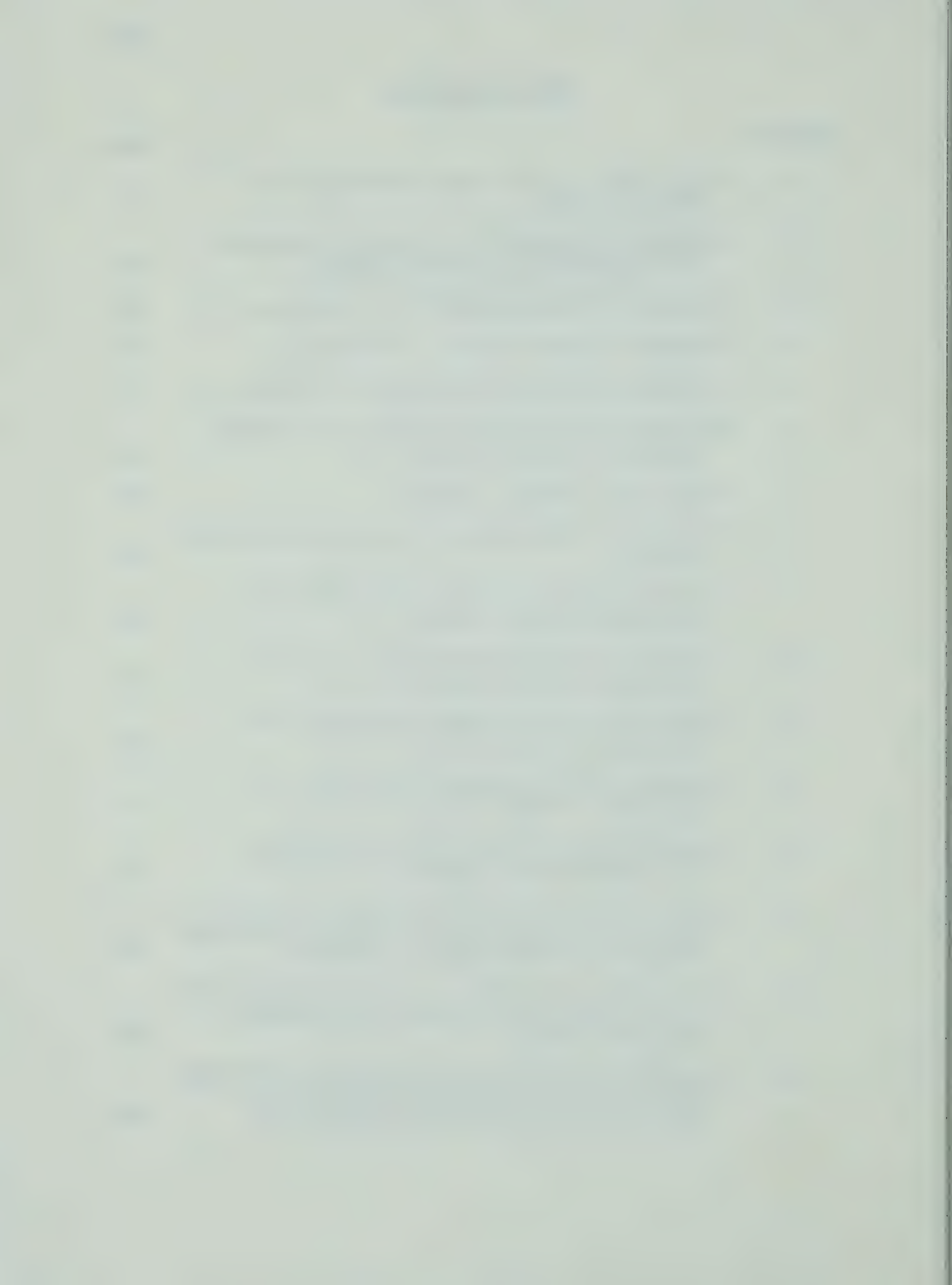


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NOMENCLATURE

a, b, c	Constants in B-W-R equation of state
A_O, B_O, C_O	Constants in B-W-R equation of state
A, B	Components in binary mixture
B	Second virial coefficient in volume expansion
B'	Second virial coefficient in pressure expansion
C	Third virial coefficient in volume expansion
C'	Third virial coefficient in pressure expansion
d	Distance
E	Electrical potential difference
E	Excess second virial coefficient
\bar{f}	Fugacity in a solution
F	Mass flow rate
H	Specific enthalpy
\bar{H}	Partial molal enthalpy
I	Current
k	Boltzmann's constant
n	Number of moles
N	Avogadro's number
Δn	Change in number of moles
p	Partial pressure
P	Pressure
P_C	Critical pressure
P_D	Pressure equivalent on diffusion in Equation (33)
P_T	Total pressure in Equation (33)
P_W	Water vapor partial pressure in Equation (33)

CHAPTER 1

The first part of the book is devoted to the study of the properties of the function $f(x)$ defined by the equation $f(x) = x^2 + 1$. We shall show that this function is strictly increasing on the interval $(0, \infty)$ and that it is concave down on the same interval. To do this, we shall use the first and second derivatives of the function. The first derivative is $f'(x) = 2x$, which is positive for $x > 0$. The second derivative is $f''(x) = 2$, which is negative for $x > 0$. Therefore, the function $f(x)$ is strictly increasing and concave down on the interval $(0, \infty)$.

In the second part of the book, we shall study the properties of the function $g(x)$ defined by the equation $g(x) = x^3 - 3x^2 + 2x$. We shall show that this function has a local maximum at $x = 1$ and a local minimum at $x = 2$. To do this, we shall use the first and second derivatives of the function. The first derivative is $g'(x) = 3x^2 - 6x + 2$, which has roots at $x = 1$ and $x = 2$. The second derivative is $g''(x) = 6x - 6$, which is negative at $x = 1$ and positive at $x = 2$. Therefore, the function $g(x)$ has a local maximum at $x = 1$ and a local minimum at $x = 2$.

The third part of the book is devoted to the study of the properties of the function $h(x)$ defined by the equation $h(x) = x^4 - 4x^3 + 6x^2 - 4x + 1$. We shall show that this function is strictly increasing on the interval $(0, \infty)$ and that it is concave up on the same interval. To do this, we shall use the first and second derivatives of the function. The first derivative is $h'(x) = 4x^3 - 12x^2 + 12x - 4$, which is positive for $x > 0$. The second derivative is $h''(x) = 12x^2 - 24x + 12$, which is positive for $x > 0$. Therefore, the function $h(x)$ is strictly increasing and concave up on the interval $(0, \infty)$.

The fourth part of the book is devoted to the study of the properties of the function $k(x)$ defined by the equation $k(x) = x^5 - 5x^4 + 10x^3 - 10x^2 + 5x - 1$. We shall show that this function is strictly increasing on the interval $(0, \infty)$ and that it is concave down on the same interval. To do this, we shall use the first and second derivatives of the function. The first derivative is $k'(x) = 5x^4 - 20x^3 + 30x^2 - 20x + 5$, which is positive for $x > 0$. The second derivative is $k''(x) = 20x^3 - 60x^2 + 60x - 20$, which is negative for $x > 0$. Therefore, the function $k(x)$ is strictly increasing and concave down on the interval $(0, \infty)$.

ΔP	Pressure drop
\dot{Q}	Rate of heat transfer
r	Distance
R	Gas constant
R	Electric resistance
T	Temperature
T_C	Critical Temperature
V	Specific volume
V	Total volume
ΔV	Volume difference
\bar{V}	Averaged volume
$\overline{\Delta V}$	Averaged volume difference
\dot{W}	Rate of work transfer
x	Composition
x	Variable
y	Subordinate variable
Y	Subordinate variable in Equation (31)
z	Compressibility factor, PV/RT

Greek

α	Constant in B-W-R equation of state
γ	Constant in B-W-R equation of state
ϵ	Characteristic energy
θ	Time
μ	Joule-Thomson coefficient
σ	Characteristic distance



ϕ	Isothermal throttling coefficient
ϕ	Potential energy
ω	Acentric factor

Subscripts

AA, BB	Pure component interaction
AB	Mixture interactions between A and B
c	Critical property
H	Constant enthalpy
i	Component in mixture
m	Mixture property
P	Constant pressure
R	Reference gas property
T	Constant temperature
x	Constant composition
1	Initial state
2	Final state

Superscripts

E	Excess property
res	Residual property
o	Zero pressure property

Symbols

*	Reduced property
<>	Average



INTRODUCTION

Information regarding the properties of materials is essential to planning and building which are the business of engineers. A large number of such data have been reported from the experimental and/or theoretical studies. But the rapid advance of technology into new fields seems always to maintain a gap between the demand for basic data and its experimental determination.

For the rational design of processes involving the transfer of heat and work accurate enthalpy data are necessary. Accurate values of enthalpy are directly useful in design but they are also needed to test theories of fluids, to improve methods of predictions, and to derive other thermodynamic properties. For certain fluids and their mixtures some enthalpy data which were obtained principally from P-V-T data, either directly using thermodynamic relations or indirectly using an equation of state, are available but those data are limited to a certain region. Particularly for the excess thermodynamic properties very few data are available.

For this reason, it is desirable to have excess enthalpies which were measured directly. It is, of course, impossible to obtain data for all the materials of interest over wide ranges of pressure, temperature, and composition; however, experimental data of selected materials and mixtures

CHAPTER 1

The first chapter of the book is an introduction to the subject of the book. It discusses the importance of the subject and the scope of the book. It also discusses the organization of the book and the notation used throughout the book. The chapter ends with a list of references.

The second chapter of the book is a review of the basic concepts of the subject. It discusses the basic definitions and the basic properties of the subject. It also discusses the basic theorems and the basic proofs of the subject. The chapter ends with a list of references.

The third chapter of the book is a review of the basic concepts of the subject. It discusses the basic definitions and the basic properties of the subject. It also discusses the basic theorems and the basic proofs of the subject. The chapter ends with a list of references.

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are useful not only in themselves, but also for derivation of other thermodynamic properties. This work was aimed to obtain data on the isothermal effect of pressure and composition on the excess enthalpy for the mixtures of hydrogen-nitrogen and nitrogen-carbon dioxide, and to analyze those results for the measurements of the effect of temperature, pressure, and composition upon excess enthalpy.

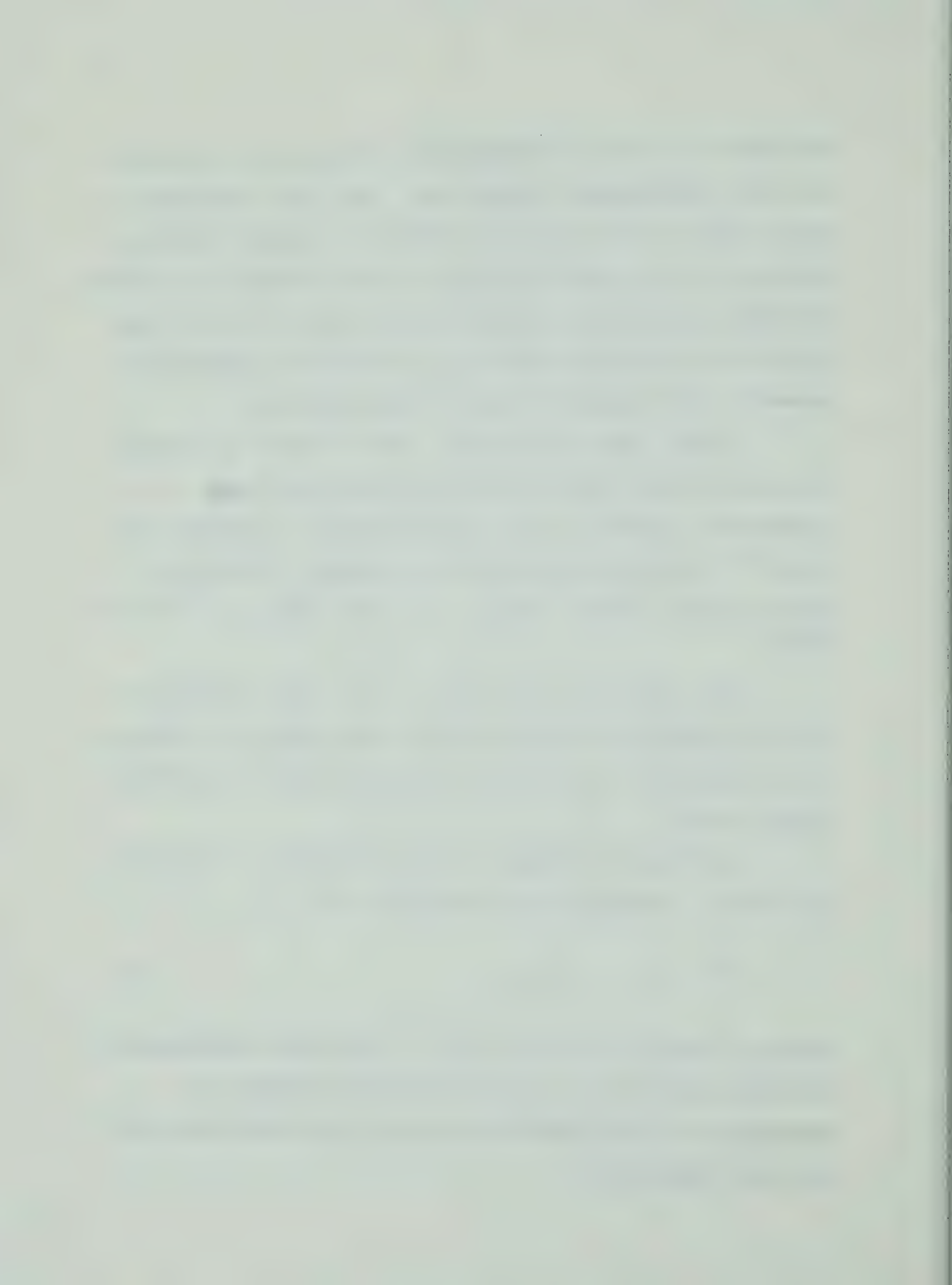
At the onset of this work, very limited and meager information was available on both experimental and theoretical aspects of the excess enthalpy of gaseous systems.^{2,8} Recently information has become available on both of these aspects through a few laboratories.^{2,20,32,33,35,55}

The scientific importance of the excess enthalpy is that it presents a stringent test of the predictive ability of an equation of state and of theories based on intermolecular forces.

The excess enthalpy, or heat of mixing, is defined at constant temperature and pressure, as:

$$H^E = H_m - \sum_i x_i H_i . \quad (1)$$

Figure 1 graphically shows that all the excess enthalpy of a binary system is the vertical distance between the enthalpy of a real mixture and that of an ideal mixture of the same composition.



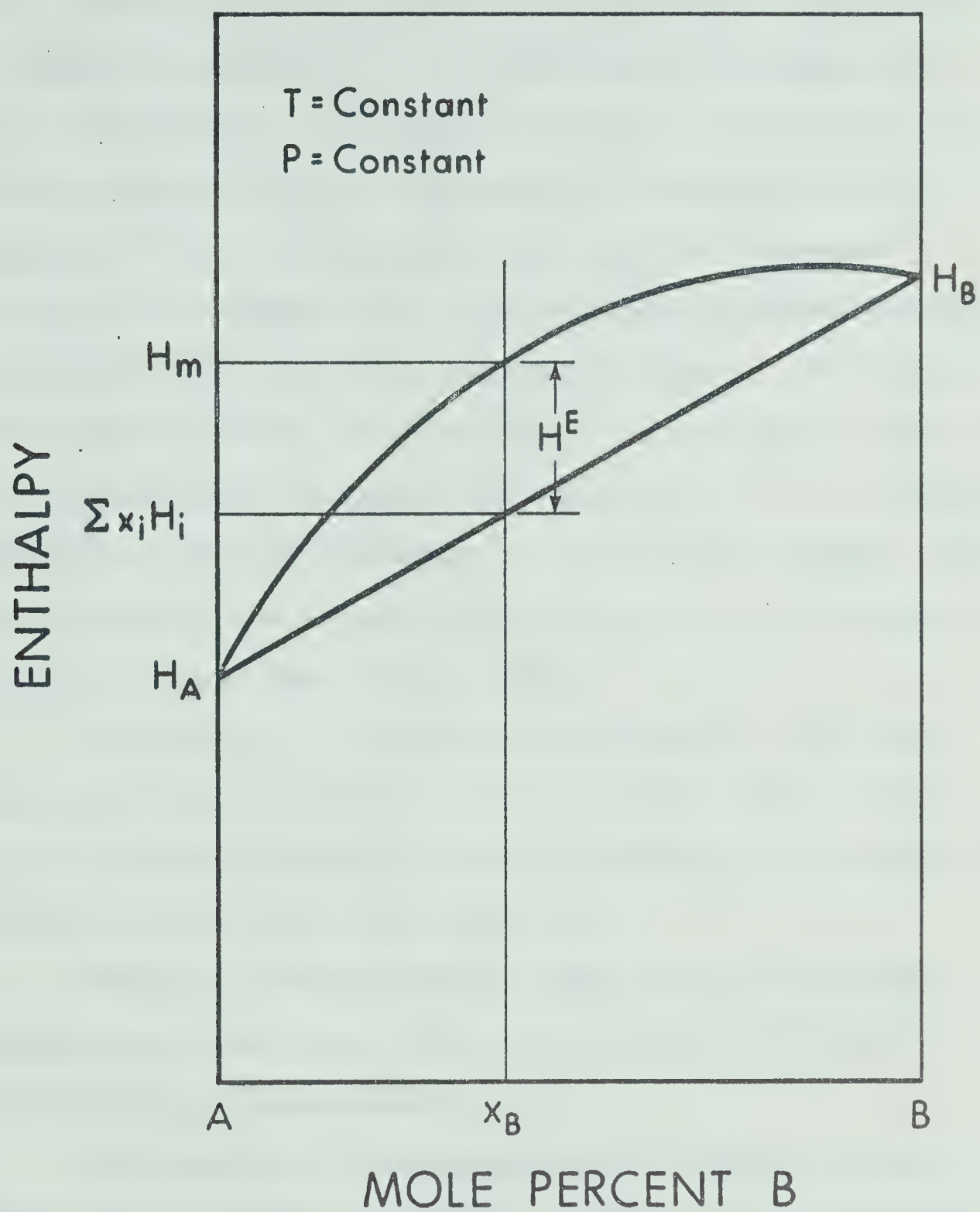


Figure 1. Definition of the Excess Enthalpy for a Binary System

Because of high accuracies required in obtaining the total properties of the mixture and its components, direct measurement of property variation is superior to investigation of total properties for studying mixing phenomena.¹ The total quantities, such as the molar enthalpy of a mixture, are also measured by experimental procedures, from the P-V-T data, for example. But these total values differ, in most cases, only slightly from the value obtained by averaging the properties of the mixture components. The measurements of the excess enthalpy will yield directly the enthalpy deviation of a multicomponent system from the ideal mixture case.

In chapter I, the basic thermodynamic relations concerned with this work, a review of the recent literature on excess enthalpy of gaseous systems, and methods of prediction of enthalpy are presented.

Chapter II describes the experimental equipment construction, measuring instruments used, and method of excess enthalpy measurements.

Comparisons of the experimental results with the literature for hydrogen-nitrogen system are considered in section A of chapter III. The virial equation of state, and corresponding states, such as correlations of Yen and Alexander⁶⁰ and liquid theories⁵⁴ are tested for their fitness for nitrogen-carbon dioxide systems in section B of the same chapter. Some analytic considerations are also

given in both sections of chapter III along with the results of this work and those of the literature.

CHAPTER I

PRELIMINARY CONSIDERATIONS

In this chapter, the thermodynamic relations which will be required in this work are presented, a review of recent experimental data is given and the methods of prediction of the enthalpy of mixtures are considered briefly. A list of all experimental work on the excess enthalpy of gaseous systems is given.

A. Thermodynamic Relations

The first law of thermodynamics, applied to a flow calorimeter with negligible potential and kinetic energy effect is:

$$\left[H_{T_2, P_2} - H_{T_1, P_1} \right]_x = \frac{\dot{Q} - \dot{W}}{F} \quad (2)$$

where \dot{Q} is the rate of heat leak, \dot{W} is the rate of electrical energy transfer, and F is the mass flow rate. Flow calorimeters may be designed for various models of operation. In the isobaric mode, the pressure difference, $P_2 - P_1$, is made small and the fluid is heated to change its temperature. Equation (2) becomes:

$$\left[H_{T_2} - H_{T_1} \right]_{P_1, x} = - \frac{\dot{W}}{F} - \int_{P_1}^{P_2} \left(\frac{\partial H}{\partial P} \right)_T dP \bigg|_{T_1} \quad (3)$$

where the integral term is the correction for the small pressure drop and heat leak is assumed to be negligible. In the isothermal mode, a pressure drop is imposed on the fluids and electrical energy is added to return the outlet temperature to that of inlet. It is possible to utilize this scheme only when the Joule-Thomson coefficient is positive, i.e., when the fluid cools upon expansion. In this case Equation (2) reduced to:

$$\left[H_{P_2} - H_{P_1} \right]_{T_1, x} = - \frac{\dot{W}}{\dot{F}} - \int_{T_1}^{T_2} \left(\frac{\partial H}{\partial T} \right)_P dT \bigg|_{P_1} \quad (4)$$

where \dot{Q} is assumed negligible and the integral term corrects for any mismatch between the inlet and outlet temperatures.

In a flow calorimeter operated in the isenthalpic mode, no energy is added to the system and the heat leak is made negligible. For this case Equation (2) reduces to:

$$\left[H_{T_2, P_2} - H_{T_1, P_1} \right]_x = 0. \quad (5)$$

The relations presented above involve integral changes in enthalpy. This integral data in a single phase region may be differentiated to yield the derivative enthalpy properties: the heat capacity, C_p , the Joule-Thomson coefficient, μ , and the isothermal throttling coefficient, ϕ . Thus:

$$C_p \equiv \left(\frac{\partial H}{\partial T} \right)_{P,x} = \lim_{\Delta T \rightarrow 0} \left[\frac{H_2 - H_1}{T_2 - T_1} \right]_{P,x} \quad (6)$$

$$\mu \equiv \left(\frac{\partial T}{\partial P} \right)_{H,x} = \lim_{\Delta P \rightarrow 0} \left[\frac{T_2 - T_1}{P_2 - P_1} \right]_{H,x} \quad (7)$$

and

$$\phi \equiv \left(\frac{\partial H}{\partial P} \right)_{T,x} = \lim_{\Delta P \rightarrow 0} \left[\frac{H_2 - H_1}{P_2 - P_1} \right]_{T,x} . \quad (8)$$

These three derivatives are related by the mathematical identity:

$$\phi = - \mu C_p . \quad (9)$$

The isothermal throttling coefficient, ϕ , can be expressed in terms of volume, temperature, and pressure as:

$$\phi = V - T \left(\frac{\partial V}{\partial T} \right)_P \quad (10)$$

thus allowing this coefficient to be obtained from compressibility data or an equation of state.

The virial expansion which is an open form of an equation of state, is a power series in density:

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots \quad (11)$$

The terms B , C , ... are known as the second, third, ... virial coefficients and they are related by the statistical theory of imperfect gases to the interactions of molecules in pairs, triples, etc.

A similar power series is an expansion in pressure:

$$\frac{PV}{RT} = 1 + B'P + C'P^2 \dots \quad (12)$$

The coefficients of two series are related by:

$$B' = B/RT \quad (13)$$

$$C' = (C - B^2)/(RT)^2. \quad (14)$$

For sufficiently low densities, the virial equation of state truncated after the second term can be expressed as:

$$\frac{PV}{RT} = 1 + B/V. \quad (11a)$$

Equation (11a) can be applied to a binary mixture and its components. From the definition of thermodynamic excess functions for a binary system:

$$V^E = V_m - (x_A V_A + x_B V_B) \quad (15)$$

and

$$B^E = B_m - (x_A B_{AA} + x_B B_{BB}) \quad (16)$$

and with the thermodynamic relations:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P \quad (10)$$

and

$$H^E = H_m - (x_A H_A + x_B H_B) \quad (1a)$$

one can show that

$$H^E = \int_0^P \left[V^E - T \left(\frac{\partial V^E}{\partial T}\right)_P \right] dP \quad (17)$$

and

$$H^E = \int_0^P \left[B^E - T \left(\frac{\partial B^E}{\partial T}\right)_P \right] dP . \quad (18)$$

Moreover, since B^E and $\frac{dB^E}{dT}$ are a function of temperature only, we have:

$$H^E = \left[B^E - T \left(\frac{dB^E}{dT}\right) \right] P. \quad (19)$$

The mixture virial coefficient, B_m , is composed of the contributions of three kinds of molecular interactions:

$$B_m = x_A^2 B_{AA} + 2x_A x_B B_{AB} + x_B^2 B_{BB} \quad (20)$$

where the coefficient B_{AB} is due to the interaction of molecules A and B, and B_{AA} and B_{BB} are due to A-A and B-B interactions, respectively,

Substituting Equation (20) into (16), we have:

$$B^E = 2x_A x_B E \quad (21)$$

where E, the excess second virial coefficient, is defined as:

$$E = B_{AB} - \frac{1}{2} (B_{AB} + B_{BB}). \quad (22)$$

Thus for low densities, since E is a function of temperature only, Equation (21) can be substituted into Equation (19) giving, for the excess enthalpy:

$$H^E = 2x_A x_B P \left[E - T \left(\frac{dE}{dT} \right)_P \right]. \quad (23)$$

The enthalpy change on mixing can be determined in a flow calorimeter by mixing two pure gases in a mixing chamber and adding electrical energy to equalize to inlet and outlet temperatures. The first law of thermodynamics for this case may be expressed as:

$$\left[H_m \right]_{T_2, P_2} - \left[\sum_i x_i H_i \right]_{T_1, P_1} = \frac{\dot{Q} - \dot{W}}{F}. \quad (24)$$

Correction may be made for the differences in pressure and temperature between the inlet and outlet. For the isobaric and the isothermal mode of Equation (24), the excess enthalpy can now be determined by:

$$H^E = \left[H_m - \sum_i x_i H_i \right]_{P,T,x} \quad (1)$$

As shown in Equation (1), needed in the calculation of the excess enthalpy are enthalpies of the pure components and that of their mixture.

B. Experimental Enthalpy Determination

The enthalpy has been obtained experimentally through the measurements of C_p , μ , ϕ as described above. Masi⁴⁰ presented a survey of these various methods for collecting enthalpy data, and a review on the Joule-Thomson effect was covered by Johnston³⁰. Potter⁴⁸ has surveyed both Joule-Thomson and isothermal throttling coefficient data.

C. Enthalpy Determination Through Empirical Methods

Since it is inconceivable that information on the physical and thermodynamic properties of all known substances and their mixtures will ever become available, it is essential to have methods to estimate and predict values for desired properties. In this regard, it is necessary that the method be subjected to and defended against reliable experimental results.

The literature presents numerous methods for estimating enthalpies of pure substances and their mixtures. A comprehensive review of prediction methods is given by Hobson and Weber,^{26,27} and recommendations on the various

correlations are discussed by Reid and Sherwood⁵². Lydersen, Greenkorn, and Hougen³⁶ have presented generalized charts based on critical properties of gases for estimating thermodynamic properties.

Various equations of state, such as the Benedict-Webb-Rubin (B-W-R)^{3,4,5}, Redlich-Kwong (R-K)⁵¹, Hirschfelder-Buehler-McGee-Sutton (H-B-M-S)^{23,24}, and the virial equations, can be used to determine enthalpies. A recent review for B-W-R, R-K, and H-B-M-S equations of state has been presented by Yorzane and Masuoka⁶². Recently Scott⁵⁴ has developed a method based on the principle of corresponding states using molecular parameters to predict properties of a system.

D. Prediction Methods of Mixture Enthalpy

For gas mixtures, deviations in behaviour from an ideal gas mixture may be caused by either or both of two effects:

- 1) the component behaviour may be nonideal, and
- 2) the interactions between components may contribute substantially to the nonideality.

It is possible for a mixture to be nonideal even though the behaviour of the individual pure components is ideal at the same temperature and pressure.

In most engineering problems, enthalpies must be generated from correlations and prediction methods. The experimental thermodynamic properties of gas mixtures have,

until recently, followed the same line as that taken for pure gases. The number of systems of interest is so large and the rate of production of experimental enthalpy data so small because of the time and effort involved that it is unlikely that experimental data are available for the problem under consideration. The ideal solution would be the calculation of thermodynamic properties, including enthalpy, from a knowledge of the interactions between molecules. At present this can only be done for relatively simple molecular models, but increasing efforts are being made in this area. For instance, Hermesen and Prausnitz²¹ and Eckert, Renon, and Prausnitz¹⁸ have calculated excess functions for binary liquid mixtures of hydrocarbons at low pressure which are in agreement with experimental values. Osborne⁴⁶ has also presented a method for the prediction of liquid mixture enthalpies from a molecular model for liquid mixing.

When attempting to determine the enthalpy of a mixture by means of a semiempirical method, one seldom has available the mixture parameters required to directly apply the model. For this reason, a prescription is required to obtain the parameters of the mixture from those of the pure materials.

Recently Nathan⁴⁴ has reviewed the types of mixture property prediction methods.

1. Pure Components

The assumption of zero heat of mixing allows the enthalpy of a mixture to be calculated from the sum of the enthalpies of the pure components present. This method may give good results at moderate pressures and relatively high temperatures, for chemically similar compounds such as hydrocarbons in a homologous series.

2. Equivalent Component Concept for Mixtures

Several methods have been proposed which consider the mixture to be a hypothetical pure component and correlate enthalpies based on a parameter such as model average boiling point, mixture molecular weight, or mixture specific gravity.

The assumption is made that a mixture and a pure component with the same correlative parameter exhibit the same enthalpy behaviour. Canjar and Peterka¹⁰ have presented correlations of this type for hydrocarbons.

3. Corresponding States

The principle of corresponding states was first applied to the correlation of P-V-T data, but the extension to enthalpies using the integrated form of Equation (10) follows directly. Among the earliest correlation of this types are those of Cope, Lewis, and Weber¹¹ and Edmister¹⁹.

Later work on generalized correlations has employed a third parameter to improve the agreement with experimental data. Lydersen, Greenkorn, and Hougen³⁶ used the compressibility factor at the critical point, z_c , while Curl and Pitzer¹⁵ employed the acentric factor, ω , which is related to the shape of the reduced vapor pressure curve. In applying these correlations to mixtures it is necessary to obtain values for the critical temperature, T_c , the critical pressure, P_c , and the third parameter of the mixture. In most cases, recourse is made to rules which allow the mixture critical properties to be calculated from those of pure components. For example, the values for a number of correlations are obtained by the linear mixing rules suggested by Kay³¹, but nonlinear mixing rules have been proposed by Pitzer and Hultgren⁴⁷, and Prausnitz and Gunn⁴⁹.

4. Enthalpies from Fugacities

The effect of temperature on the fugacity of a component in a mixture is given by:

$$\left(\frac{\partial \ln \bar{f}_i}{\partial T} \right)_{P,x} = \frac{H_i^O - \bar{H}_i}{RT^2} \quad (25)$$

and if relation for the fugacities is known, the partial molal enthalpy \bar{H}_i can be calculated. The disadvantage of this method is that any error in the expression for fugacity, which is derived from P-V-T and vapor-liquid

equilibrium data, is magnified in the differentiation. The advantage claimed for this method is that the enthalpies obtained are consistent with the vapor-liquid equilibrium data, a point of importance in multicomponent mixtures. Klein³² has used this method inversely to calculate fugacity coefficients of methane and nitrogen from their mixture enthalpies.

5. Equation of State

The enthalpy of many substances is known in the ideal gas state from spectroscopic calculations and direct experimental determinations at low pressures. With the effect of temperature on enthalpy known at zero pressure, the effect of pressure on enthalpy can be obtained from Equation (10) if an equation of state is used to represent the P-V-T behaviour of the substance.

A large number of equations of state have been proposed, but only a few have been used for extensive calculations of enthalpies. Martin³⁸ has recently reviewed equations of state primarily from the standpoint of representation of the P-V-T surface of a substance. Recently single equations like the Redlich-Kwong⁵¹ equation have been used for enthalpy prediction and the recent modification by Wilson^{58,59} is claimed to improve the accuracy of such predictions. More complex equations such as the Benedict-Webb-Rubin³ and Martin-Hou³⁹ equations have also

been used to predict thermodynamic properties including enthalpy.

A problem arises in the extension of equation of state calculation to mixtures since the constants for particular mixtures are not available and usually must be calculated from empirical mixing rules utilizing the constants of the pure components. The virial equation is one of the few equations for which the composition dependence of the constants is known exactly. This equation is restricted to vapors since the power series relation tends to diverge at densities approaching those of liquids.

E. Importance of the Excess Enthalpy

A knowledge of the precise thermal data is required for the accurate design of numerous types of process equipment and the lack of sufficiently sound data forces the design engineer to overdesign with a resultant increase in costs. The enthalpies for pure components are usually known to a good degree of accuracy, but the same is not generally true for mixtures. Accuracy in the excess enthalpy permits economical operation in gas separation, and gas purification, and cryogenic process by improved design methods.

Accurate data are difficult to determine for a multicomponent system. Even for the simplest and most common systems,

multicomponent data for fluids are almost nonexistent. Engineers and scientists required to employ such data usually must resort to simple mixture rules or correlations developed for specific situations to predict mixture methods of approximation. The validity of use of those methods is also in question when applied to the systems other than the simplest nonpolar molecules in the regions of moderate high density.

It appears then that, in the field of gaseous mixtures, there is a definite need for thermodynamic properties. Data of this type not only are of direct utility to the process industry but also can be further used to obtain valuable information of a more scientific nature.

One of the classic problems of both physics and chemistry has been that of understanding the molecular forces and their effect on gases and liquids. Because of the fact that the excess enthalpy reflects directly all of the imperfections of a solution from that of the ideal case, it is a very useful quantity for testing models based on the intermolecular forces^{50,54}.

F. Necessity of Direct Determination of Excess Enthalpy

Deriving the excess enthalpy from enthalpy data obtained through experimental methods of pure components and mixtures requires taking the differences of the total quantities, H_m and $\sum_i x_i H_i$ in Equation (1), which are in

general of the same magnitude. When the subtraction is carried out to obtain H^E , the uncertainty in the excess enthalpy is the sum of the uncertainties in the individual enthalpies. Therefore, since the excess enthalpy is small compared to the individual values used, the error introduced in obtaining H^E in this way is usually a significant percentage of the excess enthalpy value calculated. If enthalpies of pure components and their enthalpy change on mixing are available, the enthalpy of mixture is obtained from Equation (1), as:

$$H_m = \sum_i x_i H_i + H^E. \quad (26)$$

G. Background of This Work

The gaseous systems, which were investigated in this work are hydrogen-nitrogen system and that of nitrogen-carbon dioxide. These systems are ideally suited for an exploratory investigation of this nature because, from an economic viewpoint, they are cheap materials, and from a molecular point of view, since their molecules are nonpolar and simple, it fits the assumptions involved in the Lennard-Jones potential quite well²⁵. Pure component enthalpy data on both hydrogen⁹ and nitrogen^{9,16,37} are in abundance and enthalpy data are available on at least some compositions of their mixtures. A number of experimental data for the thermodynamic properties of carbon dioxide are also available easily^{9,45}. Moreover since excess enthalpy data experimentally

determined for the hydrogen-nitrogen system are available from Knoester, et al.³⁵, this system is used to test the equipment constructed for this work.

A complete review of experimental thermal data on various pure substance and mixtures was given by Mather⁴¹, and Yesavage, et al.⁶¹ Knoester, et al.³⁵ presented a compilation of thermodynamic properties, both experimental and calculated, of simple molecular gaseous mixtures, and Van Eijnsbergen and Beenakker⁵⁶ listed tabular and graphical data of thermodynamic properties for cryogenic fluids such as normal hydrogen, para hydrogen, helium, neon, nitrogen, carbon monoxide, oxygen and argon as well as methane and xenon.

Table I shows a review of all the experimental excess enthalpy data up to date for the gaseous mixtures. Theoretical determination and indirect measurement of the excess enthalpy from the other excess thermodynamic property by experiment were also published as listed in Table II.

Table IExperimental Excess Enthalpy Data for Gaseous Systems

<u>Year</u>	<u>System</u>	<u>Authors</u>	<u>References</u>
1962	Hydrogen-nitrogen	Beenakker and Coremans	1
1965	Hydrogen-nitrogen, hydrogen-argon, nitrogen-argon, methane-hydrogen, argon-methane	Beenakker, et al.	2
1967	Hydrogen-nitrogen hydrogen-argon, nitrogen-argon, hydrogen-nitrogen- argon	Knoester, et al.	35
1968	Methane-argon, methane-nitrogen, hydrogen-methane, helium-methane, helium-argon	Van Eijnsbergen and Beenakker	55
1969	Nitrogen-methane	Klein	32
1969	Nitrogen-methane	Klein, et al.	33
1970	Nitrogen-carbon dioxide	Hejmadi, et al.	20

Table II

Calculated Excess Enthalpy Data for Gaseous Systems

<u>Year</u>	<u>System</u>	<u>Authors</u>	<u>References</u>
1967	Hydrogen-nitrogen, hydrogen-argon, nitrogen-argon	Knoester, et al.	34
1968	Methane-argon, methane-nitrogen, hydrogen-methane, helium-methane, helium-argon	Van Eijnsbergen and Beenakker	56
1969	Hydrogen-nitrogen	Hsi and Lu	28

CHAPTER II

EXPERIMENTAL METHOD

In this chapter, the equipment construction, measuring and controlling instruments, and the method of measurement for the direct determination of excess enthalpy are described.

A. General Survey

The principle upon which the direct determination of the excess enthalpy based is the fact that when two different gases which are initially at the same temperature and pressure are mixed, a temperature change will occur. Since most gaseous systems have a positive excess enthalpy, heat can be supplied to the system to compensate for the cooling effect due to mixing. Hence an isothermal flow-type calorimeter is suited for these studies.

Figure 2 represents a schematic experimental method for a continuous flow system. Two pure gases A and B which are maintained at the desired pressure, pass through the heat exchanger where their temperatures are equalized and adjusted to that desired for the run. They then enter the mixing chamber. The inlet temperature, before mixing, and that of outlet, after mixing, are measured and balanced by energy input. The flow rate of the mixture, the composition, and the rate of input energy are determined. The

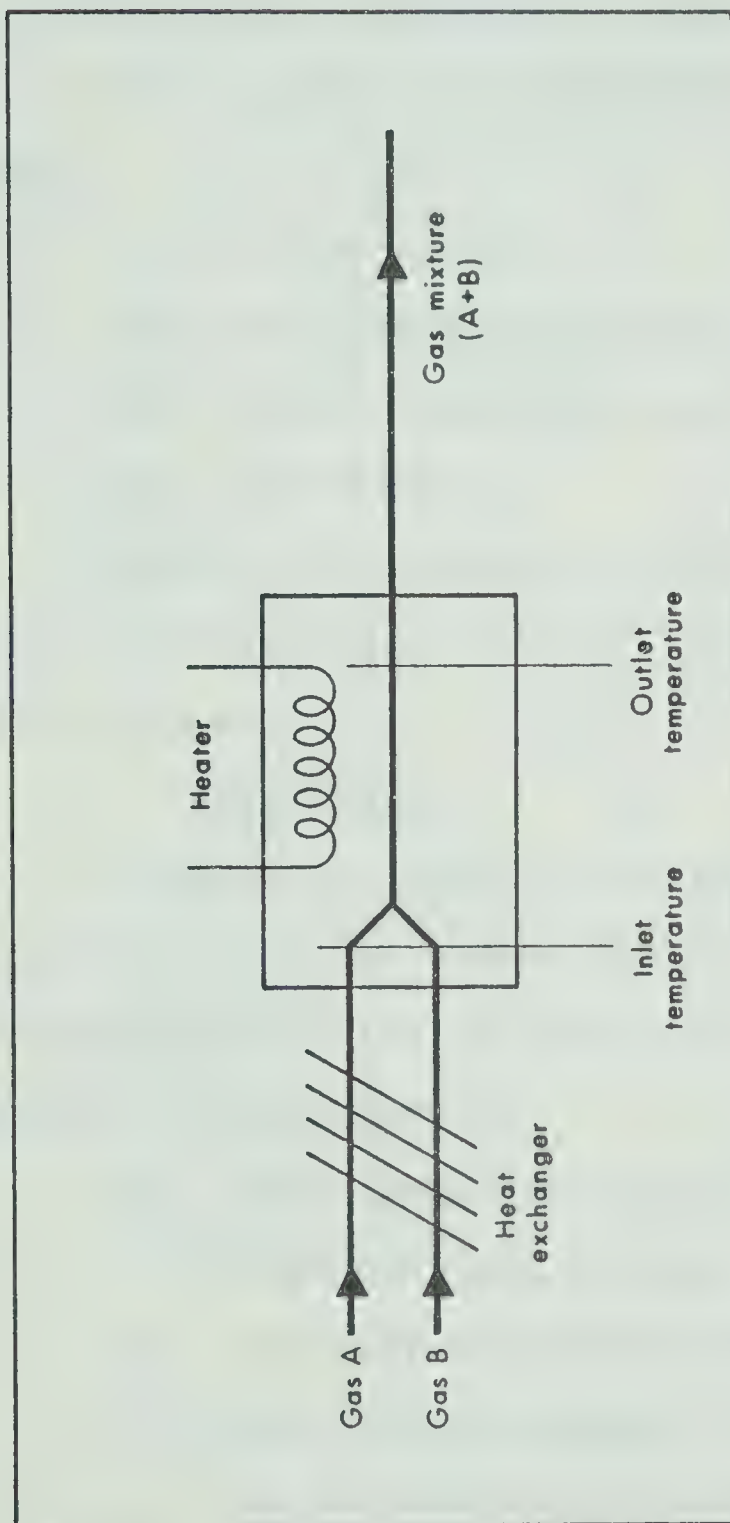


Figure 2. Schematic Diagram of the Excess Enthalpy Flow System for a Binary Mixture

heat of mixing is then calculated from the quotient of the input energy and the flow rate.

B. Experimental Equipment Construction

The apparatus is consisted of four main parts, namely,

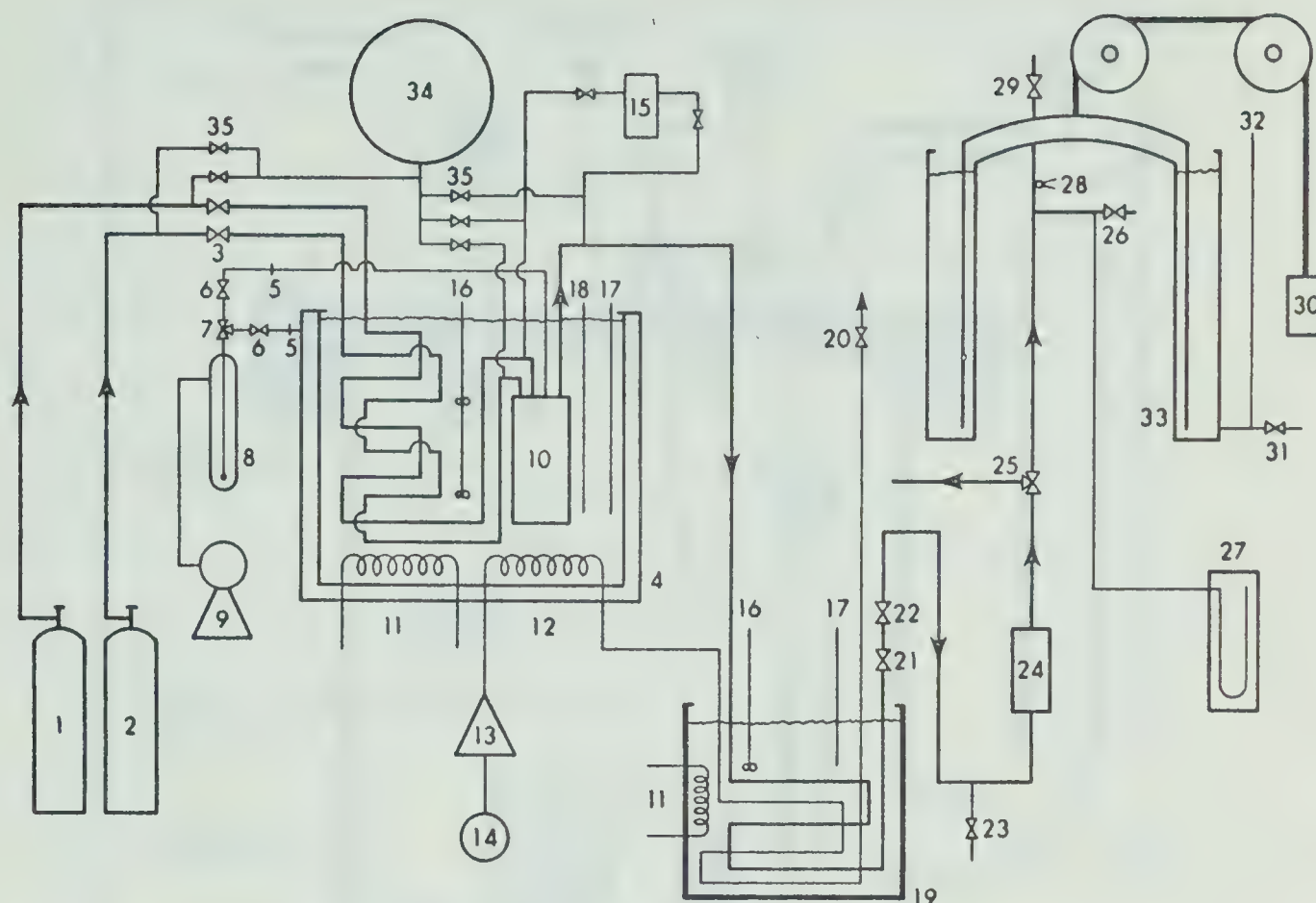
- (1) a calorimeter,
- (2) a low temperature bath,
- (3) a room temperature bath, and
- (4) a gasometer.

The detailed schematic flow diagram of the apparatus is shown in Figure 3. Details of the construction are as follows.

1. Calorimeter

As shown in Figure 4, the calorimeter which is set in a stainless steel vacuum jacket, has a mixing chamber (The detailed drawing for this is shown in Figure 27 in Appendix A) consisting of:

- (a) three concentric inner copper shells to accomplish complete mixing,
- (b) one outer stainless steel shield to minimize heat exchange between the mixing chamber and the surroundings by radiation, and
- (c) a 16-foot-long 23 gauge nichrome wire which is approximately 20 ohms at room temperature, was wrapped over the first and second copper shells for heat supply to the gas mixture.



LEGEND

- | | |
|---------------------------------------|--|
| 1. A gas Container(s) | 19. Room Temperature Water Bath |
| 2. B gas Container(s) | 20. Nitrogen Vapor Exhaust Control Valve |
| 3. Shut-off Valves for Pure Gases | 21. Shut-off Valve for Mixture Stream |
| 4. Constant Low Temperature Bath | 22. Mixture Flow Rate Regulating Valve |
| 5. Thermocouple Vacuum Gauges | 23. Sampling Valve |
| 6. Vacuum Valves | 24. Flowmeter |
| 7. Vacuum Release Valve | 25. 3-way Solenoid Valve |
| 8. Air Cold Trap | 26. Release Valve for Mixture Exhaust |
| 9. Vacuum Pump | 27. Water Manometer |
| 10. Calorimeter | 28. Thermocouple for Measuring Mixture Temperature |
| 11. Controlled Heat Input | 29. Check Valve |
| 12. Liquid Nitrogen Cooler | 30. Balancing Weight |
| 13. Liquid Nitrogen Dewar (50 l.) | 31. Water Drain Valve |
| 14. Pressure Reducer | 32. Water Level Indicator in the Gasometer |
| 15. High Pressure Mercury Manometer | 33. Gasometer |
| 16. Stirrers | 34. Heise Bourdon Tube Gauge |
| 17. Sensors for Heat Input Controller | 35. Switching Valves for Pressure Reading |
| 18. Platinum Resistance Thermometer | |

Figure 3. Schematic Flow Diagram of the Apparatus

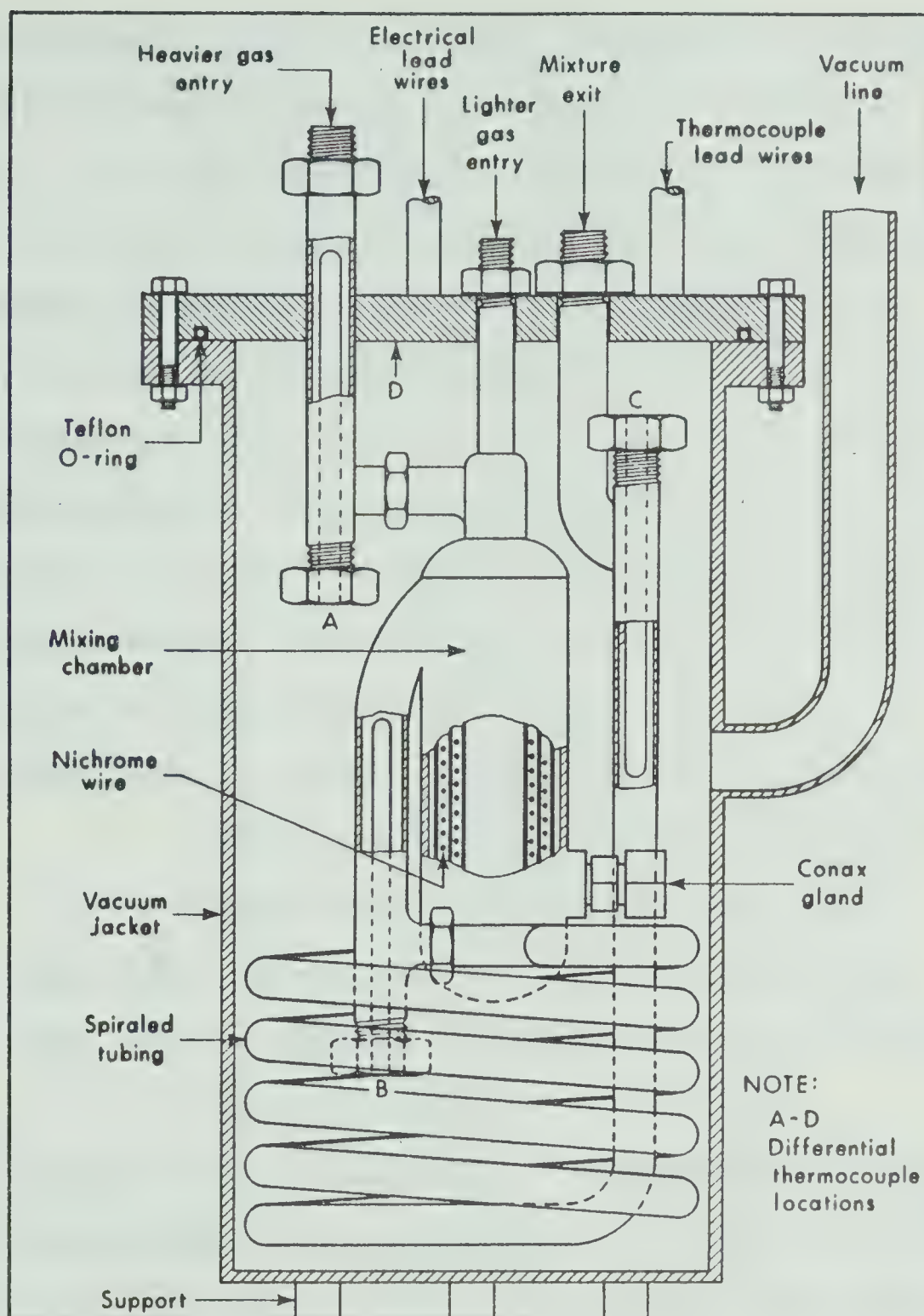


Figure 4. Schematic Diagram of the Calorimeter

Three 6-junction copper-constantan thermopiles were constructed and mounted on the calorimeter as shown in Figure 4. For this thermopile construction 40 gauge copper wire and 32 gauge constantan wire were used, and the distance between hot and cold side terminals was made $1\frac{1}{2}$ feet which is long enough for negligible small heat conduction from the hot side to the cold side through thermocouple wires. The thermopile sheath was made of 4-inch-long and $\frac{3}{16}$ -inch outside diameter thin wall stainless steel tubing. The function of each pair of these thermopiles in Figure 4 is as follows:

pair A-D: to check if inlet gases to the calorimeter have reached the same temperature as the controlled bath temperature,

pair A-B: to monitor the energy supply, and

pair B-C: to check if mixing is completed in the mixing chamber.

For the quick response to the temperature changes of the gas stream to the thermopile junctions Apiezon T was filled into the gap between thermopile sheath and the junctions. A $3\frac{1}{2}$ -foot-long $\frac{3}{8}$ -inch outside diameter stainless steel tubing was spiraled and connected by welding to the outlet of the mixing chamber and the thermopile pair B-C was mounted at both ends of this spiraled tubing.

A Conax gland was used to bring out the copper lead wires of the heater from pressurized mixing chamber to the

evacuated vacuum jacket. To bring the lead wires of the thermocouples and the heater from evacuated vacuum jacket to the atmosphere, an 8-pole vacuum seal was mounted on the 2-foot-long $\frac{1}{4}$ -inch outside diameter stainless steel tubing which was welded on the lid of the calorimeter vacuum jacket. This jacket was installed for minimizing convective and radiative heat exchange from or to the mixing chamber with surroundings. The jacket was constructed with a piece of stainless steel pipe of 9-inch-high and $4\frac{1}{2}$ -inch outside diameter. For fixing the lid, a Teflon O-ring was used with 16 stainless steel bolts to tighten.

2. Low Temperature Bath

It is necessary to maintain a constant temperature level during the experiment. For this purpose a stainless steel Dewar was constructed and insulated with styroform. The net capacity of the bath is about 67 liters. To introduce both inlet gases to the calorimeter with the equal temperature, 50-foot-long soft copper coils were installed. Beside the calorimeter jacket a platinum resistance thermometer was located to measure the absolute temperature of the bath. The temperature controller used a thermistor probe as a sensor and heaters of either 300 or 500 watts. The bath was well-stirred by a 2-stage impeller.

3. Room Temperature Bath

The temperature of gas mixture was required to be at the room temperature before it reached the regulating

valve and the gasometer. A bath of about 80 liters was installed for this end.

C. Measuring and Controlling Instruments

The major instruments to measure and control various values to determine the excess enthalpies are described briefly.

- (1) The absolute temperature in the low temperature bath was measured by a platinum resistance thermometer and a K-5 potentiometer which were calibrated by the U.S. National Bureau of Standards. Their calibration data are presented in Tables VIII and IX in Appendix B.
- (2) The pressure of the system was measured by Heise bourdon tube gauges. No difference between the dead weight gauge and the Heise gauges were found throughout the entire pressure range.
- (3) A thermocouple vacuum gauge was used to read the vacuums in the stainless steel Dewar and the calorimeter jacket. The vacuums were as good as 2 microns.
- (4) The electric energy was supplied to the gas mixture by a low voltage d-c power supply.
- (5) The input energy was measured by a 2-channel strip chart recorder which is in an error of less than 0.5 percent in full scale (including reading error).
- (6) The required time to collect the mixture in the gasometer was measured by an electric timer with an accuracy of 0.01 minute.

- (7) To read the null point of the thermopile pairs a d-c null voltmeter was used.
- (8) The pressure drop across the calorimeter was checked by a high pressure mercury manometer.
- (9) The bath temperatures were controlled within $\pm 0.05^{\circ}\text{C}$ by temperature controllers.
- (10) An 0.1 standard resistor and a 10 ohm standard resistor were used to construct the platinum resistance thermometer circuit and calorimeter heater circuit, respectively.
- (11) A 150-liter-gasometer was used to measure the mass flow rate of the gas mixture. The calibration data for the gasometer are given in Table XIII, Appendix B.
- (12) Six-junction differential thermopiles were used to investigate temperature differences. All these thermopiles indicated an error of less than ± 2 microvolts (equivalent to $\pm 0.0083^{\circ}\text{C}$) at any temperature level of this work. Therefore these were used without calibrations.

D. Method of the Excess Enthalpy Measurement

The experimental determination of the excess enthalpy was performed as follows.

Firstly the pressures in the both pure gas containers were measured.

Opening the valve of the higher pressure side, the system was filled out with that gas. Because of the gas compression effect in the system, a temperature gradient appeared in the calorimeter. It took about 4 hours to reach thermal equilibrium in the calorimeter, but opening the regulating valve to allow gas to pass through the calorimeter, reduced the time to about one hour. When thermal equilibrium is obtained, the reading of d-c null voltmeter indicates zero and at the same time this is indicated on the strip chart recorder.

When the pressure of the higher side reduced to the same pressure as that of the lower side, the valve of the lower pressure side is opened. The two pure gases flow into calorimeter and mixed there at same pressure indicated by the pressure gauge. At the same time a temperature difference occurs between inlet and outlet of the mixing chamber. This deviation is recorded on the recorder after amplification by a d-c null voltmeter. Then the required energy is supplied by a manually controlled d-c power supply, and the voltage drops across the heater in the calorimeter and the standard resistor were recorded on the two-channel recorder. From time to time the bath temperature was checked, and also the temperature of the inlet gas to the calorimeter was compared with that

of bath fluid. The mixture flow rate was controlled by a micro-regulating valve so that there was negligible pressure drop across the calorimeter.

In order to measure the flow rate of the gas mixture, the mixture is collected in the gasometer at the standard condition, and the time is measured by an electric timer. The flowmeter indicated roughly the velocity of the mixture stream. A 3-way solenoid valve was installed between the flowmeter and the gasometer to choose the flowing route of gas stream to the gasometer or to the atmosphere for vent.

All bath temperatures of each bath were controlled at their desired temperature levels by each controller. Bath fluids were water for above 0°C and 2,2,4-trimethylpentane for lower temperatures.

1. Composition Preparation

The composition of the mixture is determined by the ratio of the volumes of both pure containers combined, since those are always at the same pressure when emptying slowly during the measurements. But even if a set of known net volumes of gas cylinders is combined for the run, it is difficult to obtain a supply of constant composition mixture because the compressibilities are not the same for the different gases.

From the equation of state we have:

$$n = \frac{PV}{zRT} \quad (27)$$

When gas is released from a constant volume container at constant temperature, the change of the number of moles in the container is:

$$\Delta n = \left(\frac{P_2}{z_2} - \frac{P_1}{z_1} \right) \frac{V}{RT} \quad (28)$$

where z_1 and z_2 denote compressibility factors at pressures P_1 and P_2 at same temperature T .

But for a very small change of pressure, we may assume $z_1 = z_2$, then Equation (28) can be expressed as:

$$\Delta n = \Delta P \frac{V}{zRT} \quad (29)$$

where z is the compressibility factor at T and average value of P_1 and P_2 .

For a binary system formed with gases A and B which are supplied to be a mixture at the same pressure drop ΔP , the mole percent A in the mixture can be calculated from the following equation:

$$\text{mole \% A}(P, T_A, T_B) = \frac{V_A \cdot T_B \cdot z_B(P, T_B) \times 100}{V_A \cdot T_B \cdot z_B(P, T_B) + V_B \cdot T_A \cdot z_A(P, T_A)} \quad (30)$$

where V_A : net volume of A gas container,
 V_B : net volume of B gas container,
 T_A : absolute temperature of gas A to be supplied,
 T_B : absolute temperature of gas B to be supplied,
 $z_A(P, T_A)$: compressibility factor of gas A at P and T_A ,
 $z_B(P, T_B)$: compressibility factor of gas B at P and T_B .

2. Temperature Control and Its Measurement

To have the temperature levels lower than room temperature, liquid nitrogen was supplied into the bottom of the $\frac{1}{2}$ -inch outside diameter copper coil in the bath, boiled off after absorbing heat from the surroundings, and the gaseous nitrogen was vented to the atmosphere. To minimize consumption of coolant and the temperature fluctuation, a pressure reducer and a regulating valve were used for control of liquid nitrogen evaporating rate in the copper coil of the bath.

The absolute temperature of the bath was measured by the platinum resistance thermometer with the aid of a potentiometer and the conversion table based on the Callender equation. The circuit diagram for this measurement is shown in Figure 5. For use of the conversion table the following equation was used.

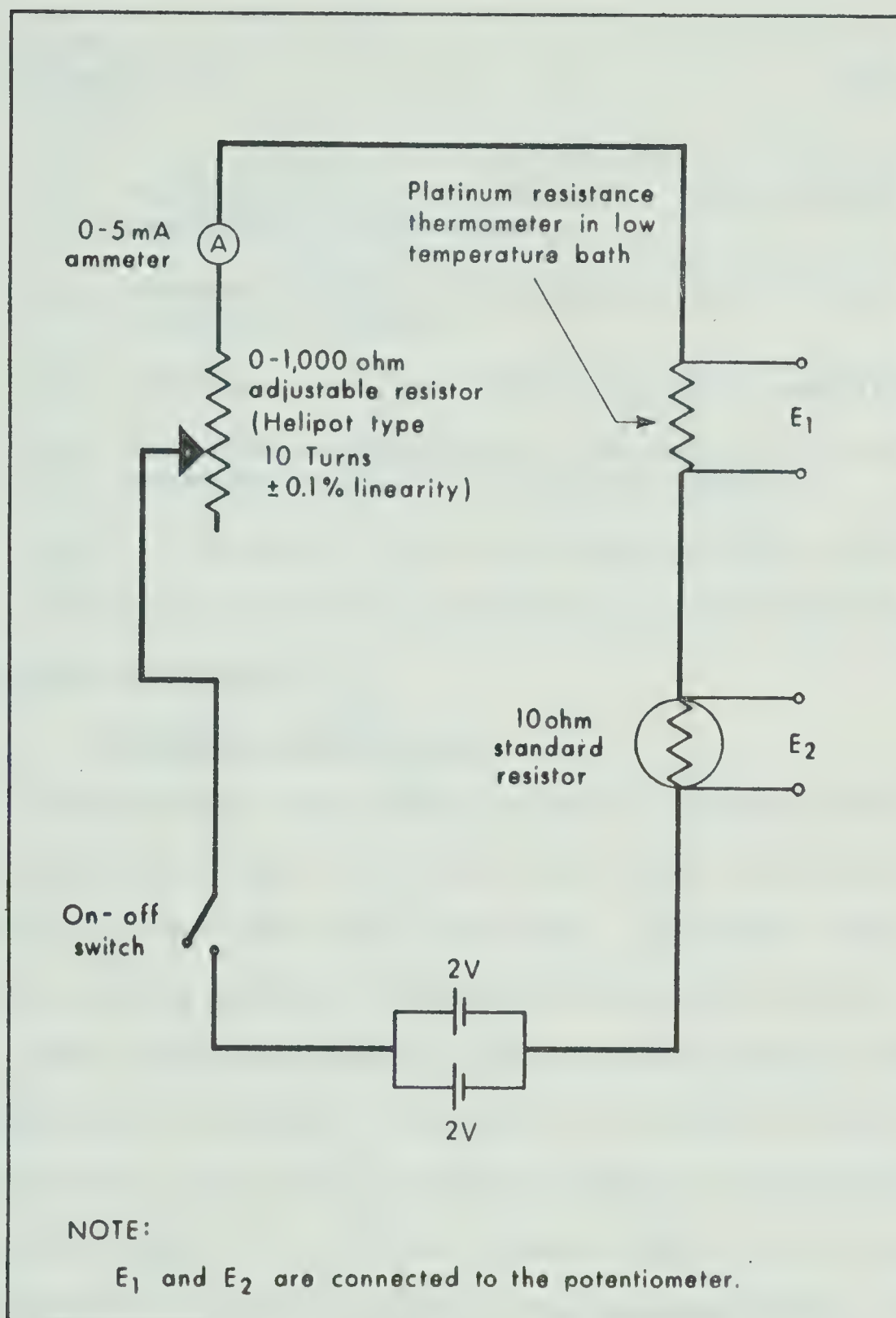


Figure 5. Platinum Resistance Thermometer Circuit

$$\frac{E_p \cdot R_s}{E_s \cdot R_p} = Y \quad (31)$$

where E_p : voltage drop in volts across the platinum resistance thermometer,
 E_s : voltage drop in volts across the 10-ohm standard resistor,
 R_s : resistance of the 10-ohm standard resistor,
 R_p : absolute resistance of platinum resistance thermometer at 0°C (= 25.564 ohms).

The Y in Equation (31) was compared with the values of the conversion table and converted to the temperature in degrees centigrade.

3. Pressure Measurement

The pressure was read by a Heise bourdon tube gauge when thermocouple pair A-B read zero, i.e., the deviation record was passed over the zero line. To obtain the exact pressure reading, actual performance was as follows:

When mixing was taking place in the mixing chamber, the temperature dropped. Then such an amount of heat was supplied such that this cooling was nearly compensated (line c in Figure 6). If the heating power is not changed, the temperature of the outlet of the mixing chamber will slowly rise (line d) because the pressure in the system decreases gradually, which means a lower gas flux and almost always a lower molar excess enthalpy. At the intersection of line d_1 with the zero line the cooling effect is compensated (measuring point 1). At this moment the

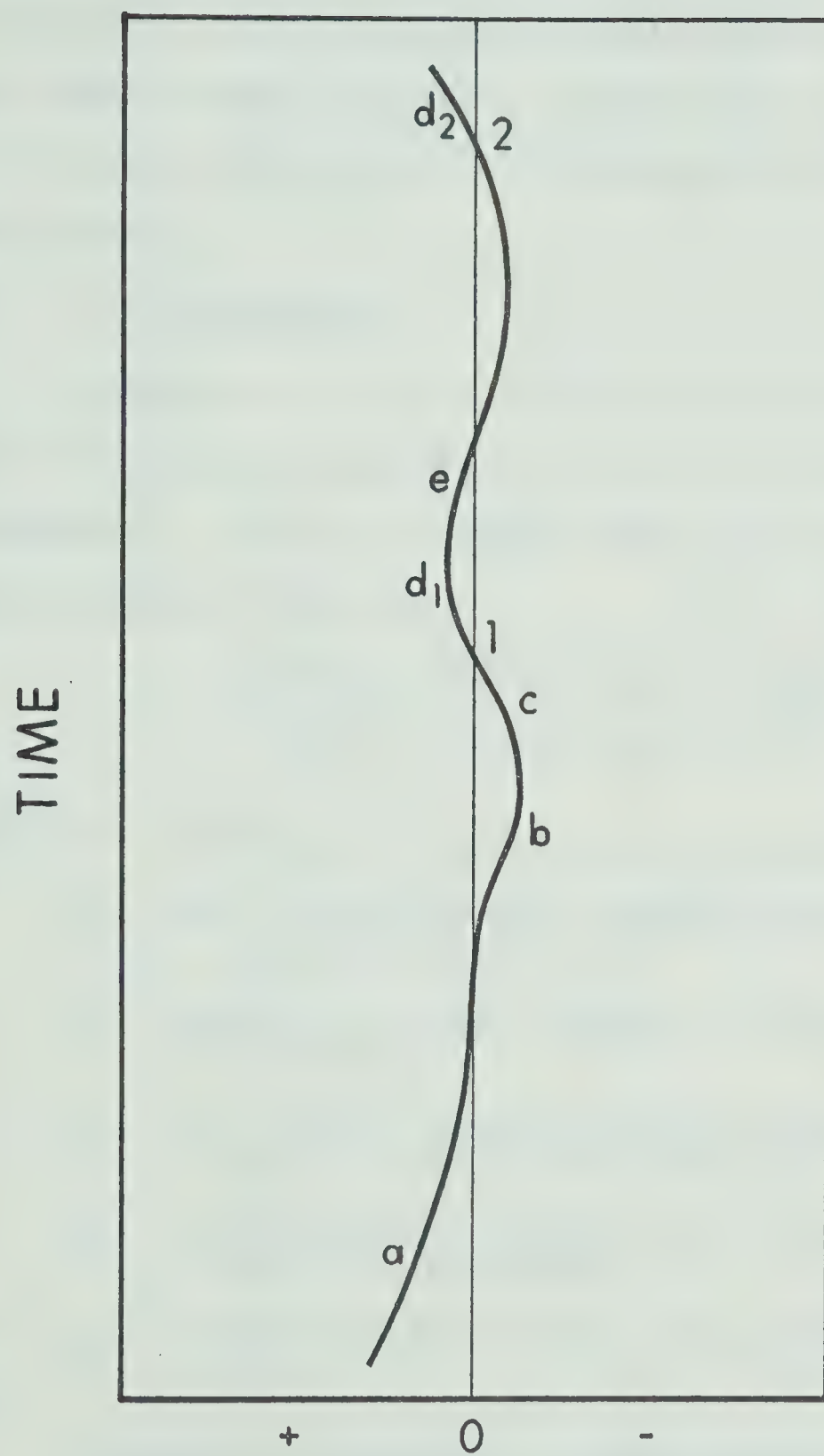


Figure 6. Differential Voltage Recording
for Energy Input to the Gas Mixture

set value of power was taken and at the same time the pressure was read. A second measurement was performed at somewhat lower pressure by diminishing the heat supply by a small amount (line e). In this way a set of data at various pressures can be obtained in a rather short time period.

4. Flow Rate

The mass flow rate of the gas mixture was measured by collecting gas mixture at a standard state in the gasometer. Following equation was established for the calculation of flow rate:

$$F = \frac{(1.6035 \times 10^{-5}) \times V_m \times d \times P_m}{(273.15 + T_m) \times z_m \times \theta} \quad (32)$$

where F: flow rate of gas mixture in gram-moles per second,

V_m : the volume in cubic centimeters for one centimeter gasometer rise,

d: gasometer rising distance in centimeters during θ seconds,

P_m : the partial pressure of the mixture in the gasometer in millimeters mercury,

T_m : temperature of the mixture collected in the gasometer in centigrade,

z_m : compressibility factor of gas mixture at T_m and P_m .

The partial pressure of the mixture, P_m , is expressed as:

$$P_m = P_T - P_W + P_D \quad (33)$$

where P_T : total pressure in the gasometer,
 P_W : partial pressure of water vapor in the
 mixture of gasometer, and
 P_D : pressure reduction equivalent due to the
 gas mixture diffusion into the water
 through the small contact area in the
 gasometer.

It was found that there was not a sensible pressure change due to the P_W and P_D . Therefore Equation (33) becomes:

$$P_m = P_T = P_{\text{barometric pressure}} \quad (34)$$

To make use of Equation (32), $V_m = 2,222 \text{ cc/cm}$ (refer to Table XIII in Appendix B) and $d = 63.1 \text{ cm}$ were chosen as constants. T_m and P_m were room temperature and barometric pressure, respectively.

5. Input Energy to the Gas Mixture

Heat dissipated across the nichrome wire in the calorimeter is measured by the circuit as shown in Figure 7. The current of the circuit can be written as:

$$I = E_2 / R_{0.1} \quad (35)$$

where I is current in amperes, E_2 voltage drop in volts across 0.1 ohm standard resistor ($R_{0.1} = 0.1 \text{ ohm}$).

Then the power, \dot{W} , in Joules per second, is expressed as:

$$\dot{W} = I \times E_1 \quad (36)$$

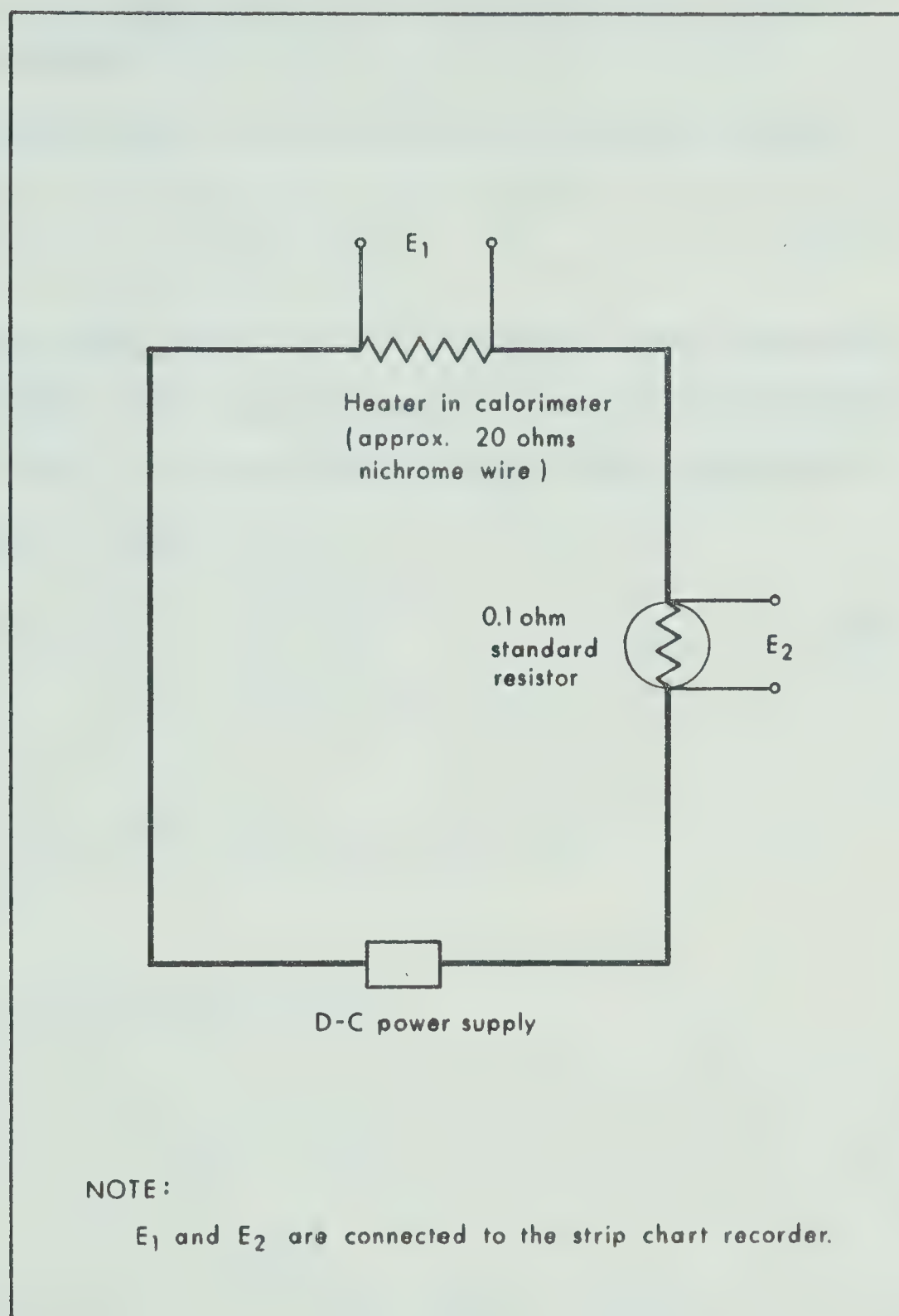


Figure 7. Calorimeter Heater Circuit

where E_1 is voltage drop in volts across the heater in the calorimeter.

Combination of Equations (35) and (36) gives:

$$\dot{W} = (10) \times E_1 \times E_2 . \quad (37)$$

Since the excess enthalpy, H^E , in Joules per gram-mole, is calculated from the quotient of the input energy and the flow rate, or from Equations (24) when neglected heat leak, we have:

$$H^E = \frac{\dot{W}}{F} . \quad (38)$$

CHAPTER III

EXPERIMENTAL RESULTS AND THEIR ANALYSIS

This chapter covers the experimental results of this work, comparisons with the literature, and data analysis.

Presented in section A for hydrogen-nitrogen system are the smoothed excess enthalpy data, comparisons with the literature, and their interpretation.

In section B experimental results for nitrogen-carbon dioxide system are reported, and comparisons are made with the virial equation of state truncated after the second term, the B-W-R equation of state and the corresponding state correlations of Yen and Alexander⁶⁰ and liquid theories⁵⁴.

A. Hydrogen-Nitrogen System

The direct determination of the excess enthalpy of the hydrogen-nitrogen system has been covered over the pressure range of 5 to 130 atm., the temperatures of nominal 20, 7, -3, and -73°C, and for the compositions of nominal 26, 51, and 76 mole percent nitrogen. The experimental raw data of the excess enthalpy as a function of pressure and composition, are presented in Table XVII in Appendix D. A detailed example for the calculation of the excess enthalpy from the experimental measurements is given in Appendix E.

1. Material Used

The sources and purity of the gases used are given in Table III. The gases were used without further purification.

2. Experimental Work

The experimental method was followed as the same way described in section D of previous chapter.

The pressure of the hydrogen containers was between 1,800 and 2,000 pounds per square inch and that of nitrogen containers between 2,100 and 2,300. Both pure gas containers were at room temperature. They were regular standard commercial gas cylinders HK (calculated as 1.51 cubic feet in net volume) for hydrogen and K (calculated as 1.52 cubic feet in net volume) for nitrogen.

Composition Preparation

For the hydrogen-nitrogen system, since for both pure gases their compressibility changes with pressure at constant temperature are almost linear, the composition was determined by calculation method.

Since both pure gas cylinders are set in the same room temperature, Equation (30) reduces to:

$$\text{Mole \% nitrogen (P,T)} = \frac{V_{N_2} \cdot z_{H_2}(P,T) \times 100}{V_{N_2} \cdot z_{H_2}(P,T) + V_{H_2} \cdot z_{N_2}(P,T)} \quad (39)$$

Table III

Sources and Purity of the Gases Used for the
Hydrogen-Nitrogen System

(1) Nitrogen (High Purity)

Supplier: Consumer's Welding Co.

Typical Analysis Data:

nitrogen	99.993%
oxygen	20 ppm
carbon dioxide	5 ppm
hydrogen	5 ppm
moisture	15 ppm
argon	100 ppm
maximum total impurities (non-inert)	40 ppm

(2) Hydrogen

Supplier: Canadian Liquid Air Co., Ltd.

Typical Analysis Data

hydrogen	99.992%
	(as remainder)
oxygen	46 ppm
nitrogen	31 ppm
hydrocarbon	no detected
carbon dioxide	no detected

(3) Nitrogen (Low Purity)*

Supplier: Canadian Liquid Air Co., Ltd.

Purity: 99.7%

*Use for investigation of impurity effect on excess enthalpy.

For various compositions the cylinders were combined as ratios of number of nitrogen cylinder to that of hydrogen being 1 to 3, 1 to 1, and 3 to 1 for nominal 26, 51, and 76 mole percent nitrogen, respectively.

Variations of composition with pressure for each combination are shown in Figure 8, which were calculated by Equation (39). For this computation the compressibility factors were calculated from the experimental P-V-T data of Wiebe and Gaddy⁵⁷ for the hydrogen-nitrogen mixtures, of Din¹⁶ for nitrogen, and of Michels, et al.⁴² for hydrogen. Table IV shows comparisons of the composition with the determination by a gas chromatograph.

Table IV

Comparisons of Compositions Determined by Calculation and
by Gas Chromatograph

<u>Pressure (atm)</u>	<u>Mole Percent Nitrogen</u>		<u>Deviation</u>
	<u>Calc. by Eq. (39)</u>	<u>Gas Chromatograph</u>	
75.8	26.02	25.85	+0.65%
115.8	76.25	76.00	+0.33%

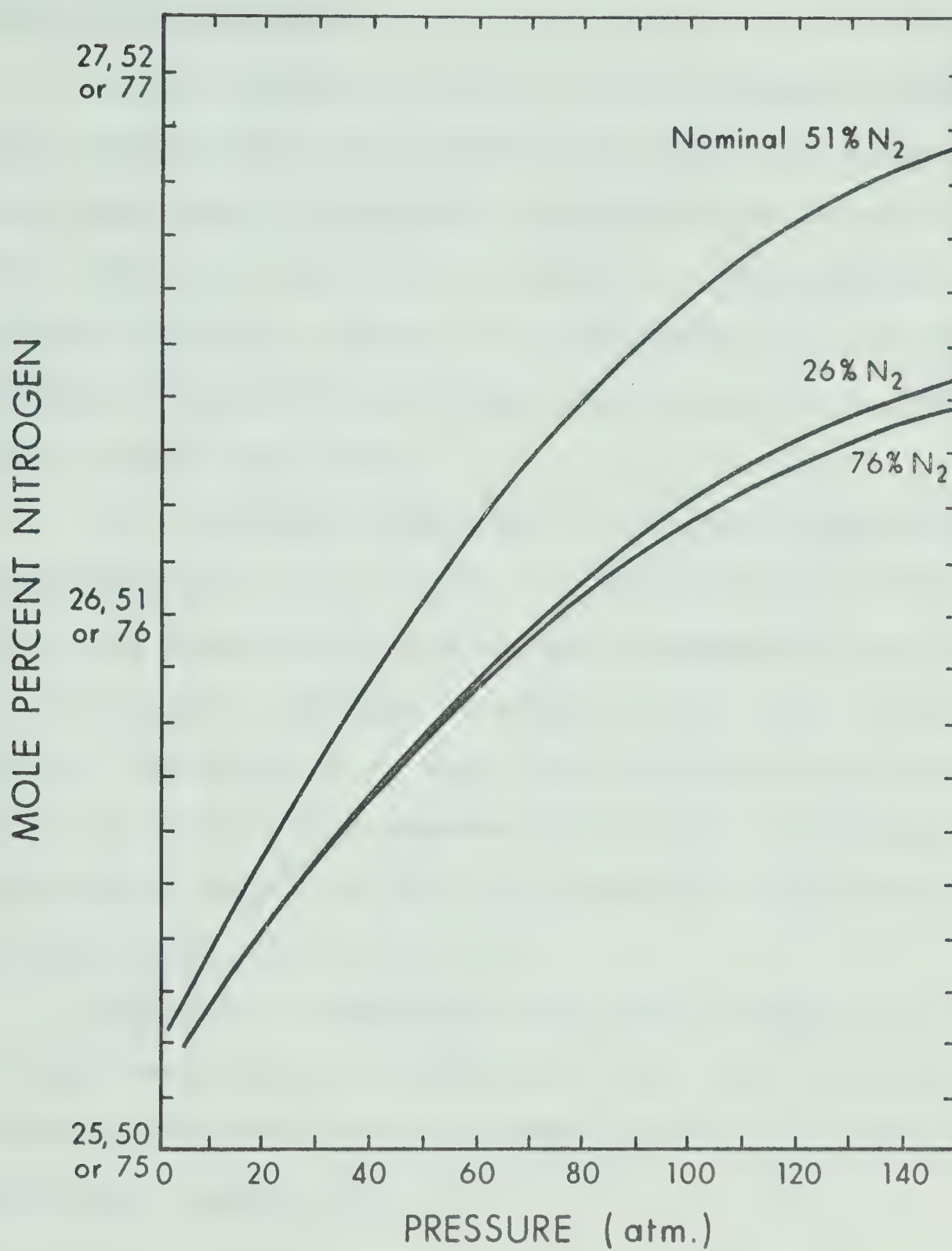


Figure 8. Composition Variations for Hydrogen-Nitrogen System

Flow Rate Calculation

To use Equation (32) for the calculation of flow rate, measurements are needed for barometric pressure, P , room temperature, T , mixture compressibility factor at P and T , and time required, θ , to fill out the gasometer with mixture, since the volume of the gasometer, V_m , for one centimeter rising of it and the rising distance, d , are fixed as mentioned above.

The barometric pressure, P , and room temperature, T , were varied with ± 0.1 percent of their absolute values during the experiment. And mixture compressibility factor, z_m , at standard condition is also constant, i.e., $z_m = 0.9988$. The error of z_m when taken as above is no larger than 0.15 percent when compared with Wiebe and Gaddy's experimental data⁵⁷ or with calculated data from the virial equation of Hilsenrath, et al.²²

Therefore to determine flow rate in this way, θ is the only variable in the Equation (32). The flow rate calculated as such way, was ranged between 0.02 and 0.12 gm-mole per second.

3. Reproducibility of Data and Data Smoothing

The data for the hydrogen-nitrogen system were reproduced with 1 percent for the entire experimental pressure range for each temperature level. No dependence of H^E on the mass flow rate was found in this work.

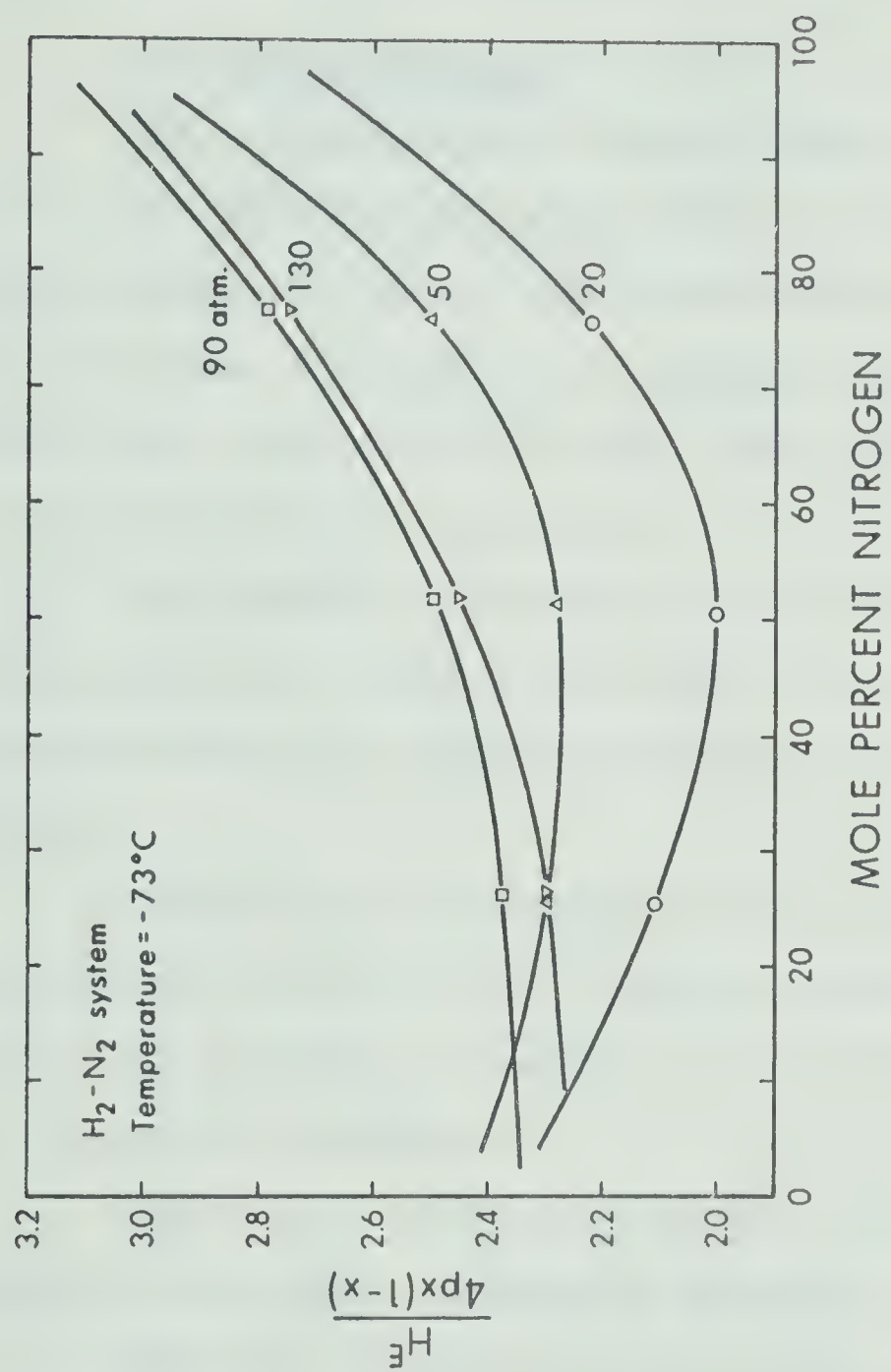


Figure 9. Graphical Method of Data Smoothing for Hydrogen-Nitrogen System

All data were smoothed by graphical method drawing $H^E/4px(1-x)$ against x . The typical illustration is shown in Figure 9 for the temperature of -73°C .

4. Error Analysis

The errors involved in this data are as follows.

The temperatures were controlled within $\pm 0.05^{\circ}\text{C}$ for each temperature level. This can introduce an error in the excess enthalpy of 0.1 percent, which can be determined from the Figures 16 and 17, the temperature dependence of the excess enthalpies.

The pressure is read within 1 pound per square inch error which may introduce an error of 0.07 percent for high pressure and 0.2 percent low pressures on the excess enthalpy values.

Composition determined by calculation or by analysis may include an error of 0.7 percent themselves which, from Figure 13, introduce an error on the excess enthalpies of 1.5 percent in maximum.

Due to the calculation of flow rate the maximum error on the excess enthalpies becomes 1.5 percent.

The error on the excess enthalpies due to input energy calculation was about 0.5 percent.

The errors due to the impurity in the pure gases, the time lag for the reading gauges, the pressure drop across the calorimeter and heat leak were negligibly small.

Therefore the total error introduced on the excess enthalpy determination from the above sources becomes less than 4 percent.

5. Smoothed Data and Comparisons with the Literature

The smoothed data are given in Table V for each temperature level studied in each 10 atm. and 10 mole per cent of nitrogen. For the comparison with the literature, for 25, 52.5, and 78 mole percent nitrogen at 20 and -73°C , and for 95 atm. at 7, -3 , and -73°C smoothed data were also listed.

Comparisons with the results of Knoester, et al.³⁵ are presented in Figures 10 and 13. Another source of the excess enthalpy data for this system is of the work of Hsi and Lu²⁸. They calculated the excess enthalpies of hydrogen-nitrogen system from the experimental excess volume data of Zandbergen and Beenakker⁶³ using Equation (17). Figures 11, 12 and 13 show comparisons with Hsi and Lu's work²⁸.

The agreement between this work and that of Hsi and Lu is within 5 percent and with that of Knoester, et al. is within 3 percent. (Note: The data of Knoester, et al. are available at -72°C . Therefore they were corrected to -73°C for comparison with the results of this work).

6. Data Analysis

From a theoretical point of view, one is confronted with the difficult situation of presenting and describing a system that will cover a wide range of densities. For

Table V
Smoothed Excess Enthalpies of Hydrogen-Nitrogen System
(Unit: Joules/gm-mole)

1. Nominal 20°C		Mole Fraction of Nitrogen											
Pressure (atm.)	(0.10)	(0.20)	(0.25)	(0.30)	(0.40)	(0.50)	(0.525)	(0.60)	(0.70)	(0.78)	(0.80)	(0.90)	
10	4.5	7.4	8.5	9.3	10.3	10.5	10.5	10.1	8.9	7.4	7.0	4.0	
20	7.9	14.0	16.3	18.2	20.6	21.3	21.2	20.3	17.6	14.3	13.3	7.4	
30	12.0	21.2	24.7	27.5	31.1	32.0	31.9	30.4	26.3	21.3	19.8	11.0	
40	15.4	27.5	32.3	36.2	41.4	43.0	42.9	41.1	35.6	28.8	26.7	14.6	
50	19.0	34.1	40.2	45.2	51.8	54.0	53.8	51.5	44.4	35.2	32.6	17.4	
60	22.2	40.4	47.8	53.9	62.3	65.0	64.8	62.1	53.5	42.9	39.7	21.6	
70	25.8	46.9	55.5	62.7	72.4	75.6	75.3	72.0	61.9	49.4	45.8	24.6	
80	29.7	53.6	63.1	71.1	81.9	85.6	85.4	81.9	71.0	57.2	53.1	29.1	
90	33.4	60.1	70.7	79.5	91.3	95.1	94.8	91.0	79.1	64.0	59.5	32.9	
100	37.3	66.8	78.5	88.1	101.0	105.2	104.8	100.7	87.7	71.3	66.4	36.9	
110	40.6	72.8	85.6	96.1	110.2	115.1	114.8	110.5	96.5	78.5	73.1	40.8	
120	43.9	78.8	92.7	104.2	119.7	125.0	124.8	120.3	105.1	85.8	79.9	44.8	
130	48.0	85.5	100.4	112.6	129.0	134.7	134.3	129.5	113.7	93.1	86.9	49.0	
2. Nominal 7°C													
10	4.7	7.8	-	9.8	10.8	11.0	-	10.4	9.0	-	6.9	3.9	
20	8.2	14.7	-	19.4	22.2	23.0	-	21.9	18.9	-	14.1	7.6	
30	12.6	22.0	-	28.6	32.3	33.4	-	32.1	28.2	-	21.8	12.5	
40	16.6	29.4	-	38.5	44.0	46.0	-	44.5	39.5	-	30.6	17.6	
50	21.0	37.0	-	48.2	54.8	57.0	-	54.9	48.3	-	37.2	21.2	
60	24.9	44.2	-	58.0	66.2	69.1	-	66.5	58.4	-	44.6	25.2	
70	28.5	50.7	-	66.7	76.5	80.1	-	77.4	68.4	-	52.9	30.2	
80	31.4	56.8	-	75.5	87.5	92.0	-	88.9	78.2	-	59.7	33.6	
90	36.8	65.4	-	86.0	98.5	103.0	-	99.5	87.8	-	67.6	38.6	
95	38.4	68.5	-	90.3	103.9	108.9	-	105.4	93.0	-	71.6	40.7	
100	39.1	70.5	-	93.8	108.6	114.4	-	111.0	97.9	-	75.1	42.5	
110	42.9	77.8	-	103.6	119.8	125.6	-	121.2	106.4	-	81.2	45.6	
120	48.1	85.6	-	112.7	129.6	136.0	-	131.9	117.1	-	90.8	52.1	
130	55.6	97.2	-	126.1	143.5	149.9	-	145.9	130.8	-	103.3	60.8	

Table V (Continued)

3. Nominal -3°C		Mole Fraction of Nitrogen										
Pressure (atm.)	(0.10)	(0.20)	(0.25)	(0.30)	(0.40)	(0.50)	(0.525)	(0.60)	(0.70)	(0.78)	(0.80)	(0.90)
10	4.3	7.7	-	10.0	11.5	12.0	-	11.5	10.1	-	7.7	4.4
20	9.4	16.2	-	20.9	23.6	24.5	-	23.5	20.6	-	15.8	9.0
30	14.2	24.7	-	31.8	35.8	37.0	-	35.5	31.1	-	23.9	13.5
40	17.9	31.8	-	41.9	47.9	50.0	-	48.1	42.1	-	32.2	18.1
50	22.9	40.4	-	52.5	59.7	62.1	-	59.7	52.4	-	40.2	22.8
60	26.4	47.3	-	62.5	71.8	75.1	-	72.1	63.1	-	48.0	26.9
70	30.9	54.9	-	72.1	82.6	86.5	-	83.8	74.1	-	57.3	32.7
80	35.3	62.7	-	82.3	94.2	98.5	-	95.4	84.5	-	65.3	37.3
90	39.2	70.2	-	92.6	106.4	111.1	-	106.5	92.8	-	70.1	38.9
95	41.8	74.5	-	97.9	112.1	117.0	-	112.8	99.1	-	75.9	42.9
100	43.5	77.6	-	102.2	117.1	123.0	-	118.8	104.8	-	80.5	45.6
110	45.8	83.2	-	111.3	129.1	136.0	-	131.4	115.3	-	87.8	49.3
120	51.6	92.6	-	122.8	141.6	148.6	-	143.4	126.2	-	96.5	54.5
130	47.1	97.3	-	133.7	156.1	164.1	-	157.9	137.7	-	104.2	57.9
4. Nominal -73°C												
10	6.1	11.6	13.9	15.9	18.8	20.0	20.0	19.4	17.0	13.8	12.8	7.1
20	16.3	27.5	31.7	35.0	39.4	41.0	41.0	40.1	36.4	30.9	29.2	17.4
30	25.4	43.0	49.5	54.6	61.3	64.0	64.1	62.9	57.4	49.3	46.4	27.9
40	31.6	55.6	64.9	72.6	83.3	88.0	88.3	87.2	79.8	67.9	64.0	38.2
50	43.4	74.6	86.4	97.1	108.6	114.0	114.2	107.4	102.2	87.1	82.2	49.3
60	51.6	89.9	104.8	116.6	132.9	139.8	140.0	137.8	126.2	108.3	102.2	61.6
70	59.8	105.5	123.7	138.8	160.1	169.5	170.3	167.8	152.9	130.1	122.7	73.1
80	67.6	120.6	142.0	159.8	185.5	197.5	198.4	195.7	178.8	152.2	143.5	85.6
90	76.5	136.1	160.0	180.3	209.3	223.2	224.4	222.2	203.5	173.6	163.6	97.5
95	79.7	142.9	168.6	190.3	221.6	237.0	238.2	235.7	215.8	184.2	173.8	103.8
100	83.2	149.2	176.3	199.1	231.9	248.7	250.3	248.2	228.1	195.1	184.0	109.9
110	90.5	162.6	192.2	217.1	253.5	272.7	274.3	272.4	250.4	214.3	202.0	120.4
120	98.1	176.3	208.1	235.3	274.9	294.5	296.4	293.9	270.1	231.6	218.8	131.3
130	105.4	189.4	223.4	252.4	294.9	316.2	316.3	315.7	289.5	247.2	233.0	138.9

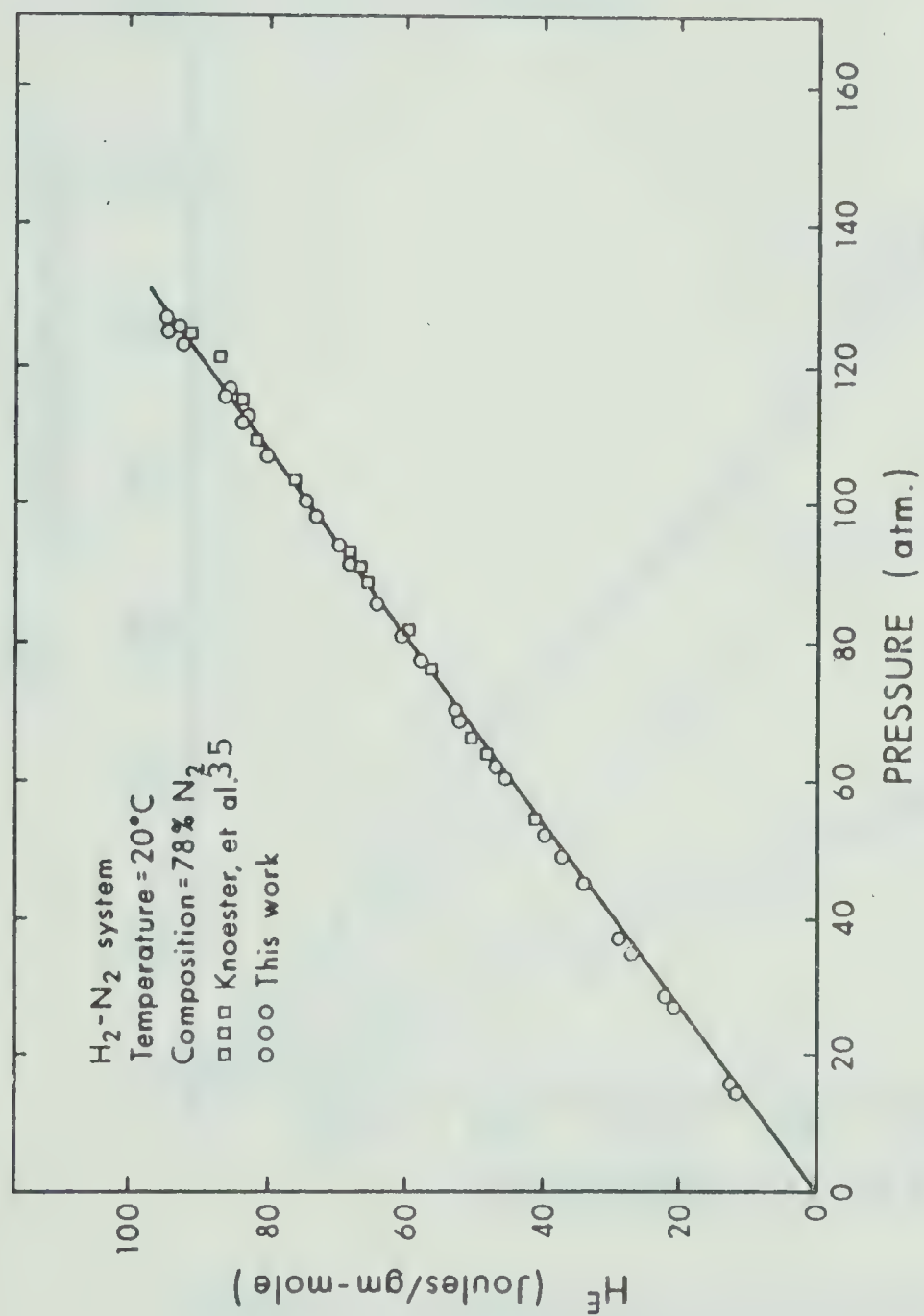


Figure 10. Comparison of the Excess Enthalpies for Hydrogen-Nitrogen System at 20°C

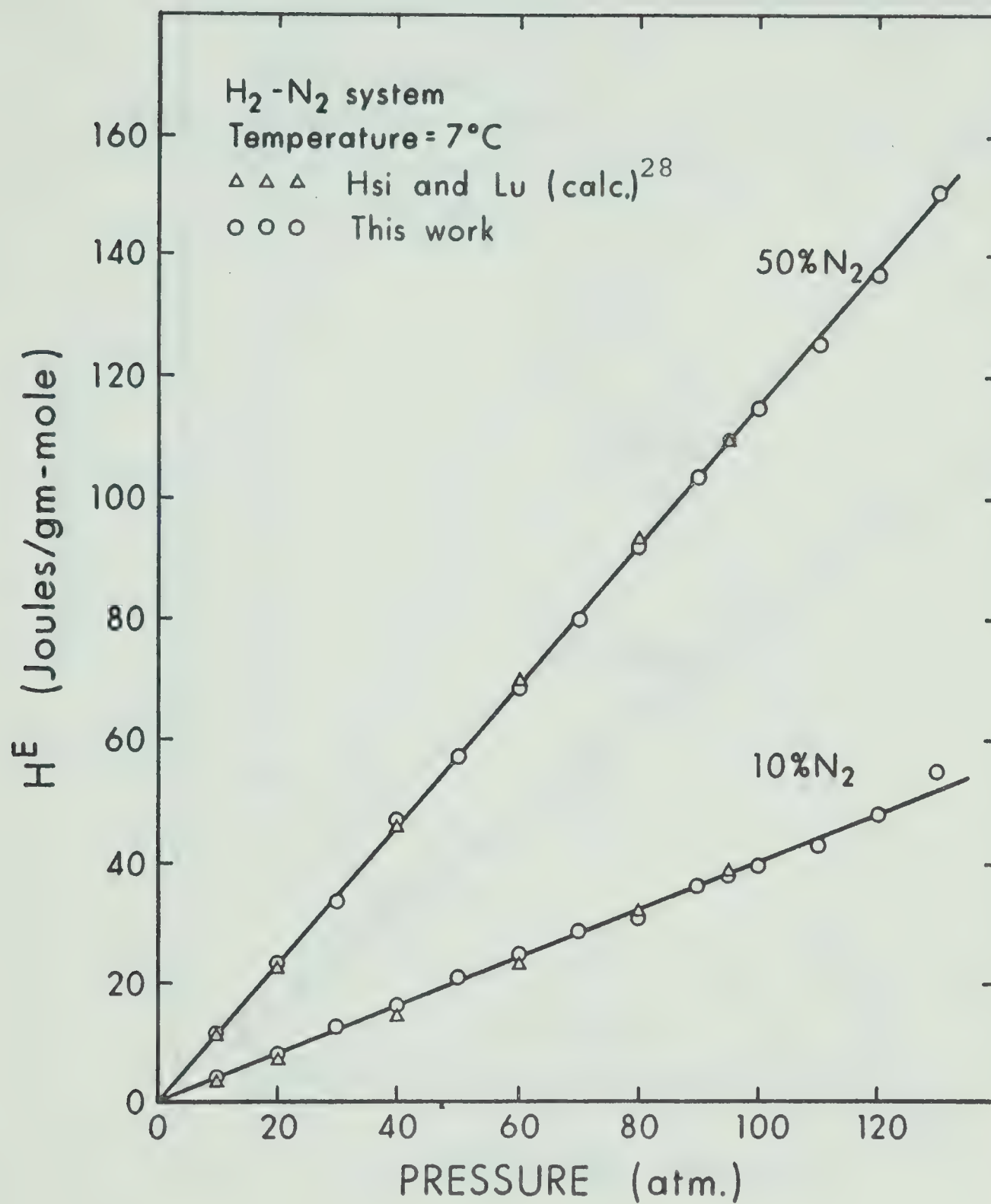


Figure 11. Comparison of the Excess Enthalpies for Hydrogen-Nitrogen System at $7^\circ C$

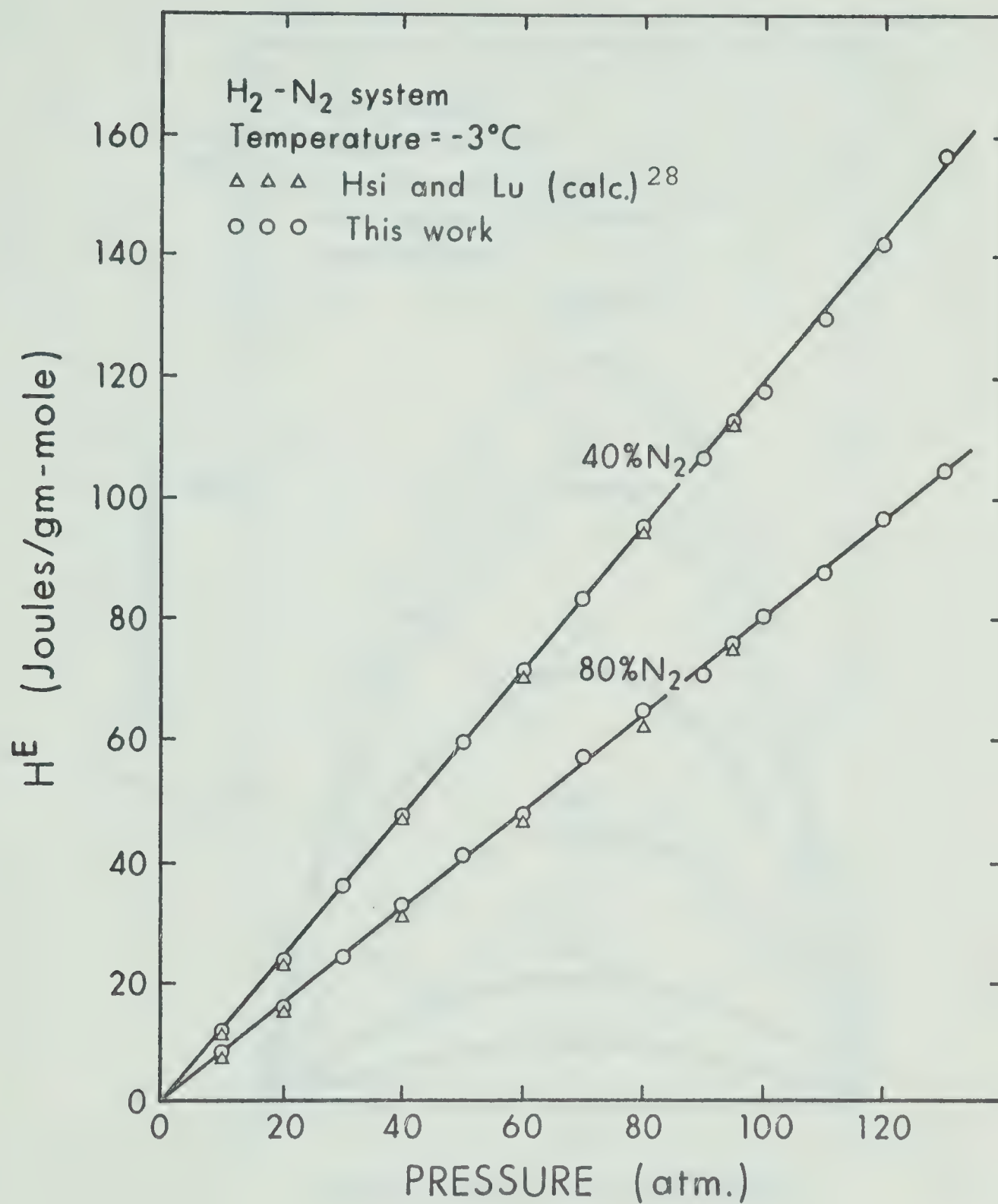


Figure 12. Comparison of the Excess Enthalpies for Hydrogen-Nitrogen System at $-3^\circ C$

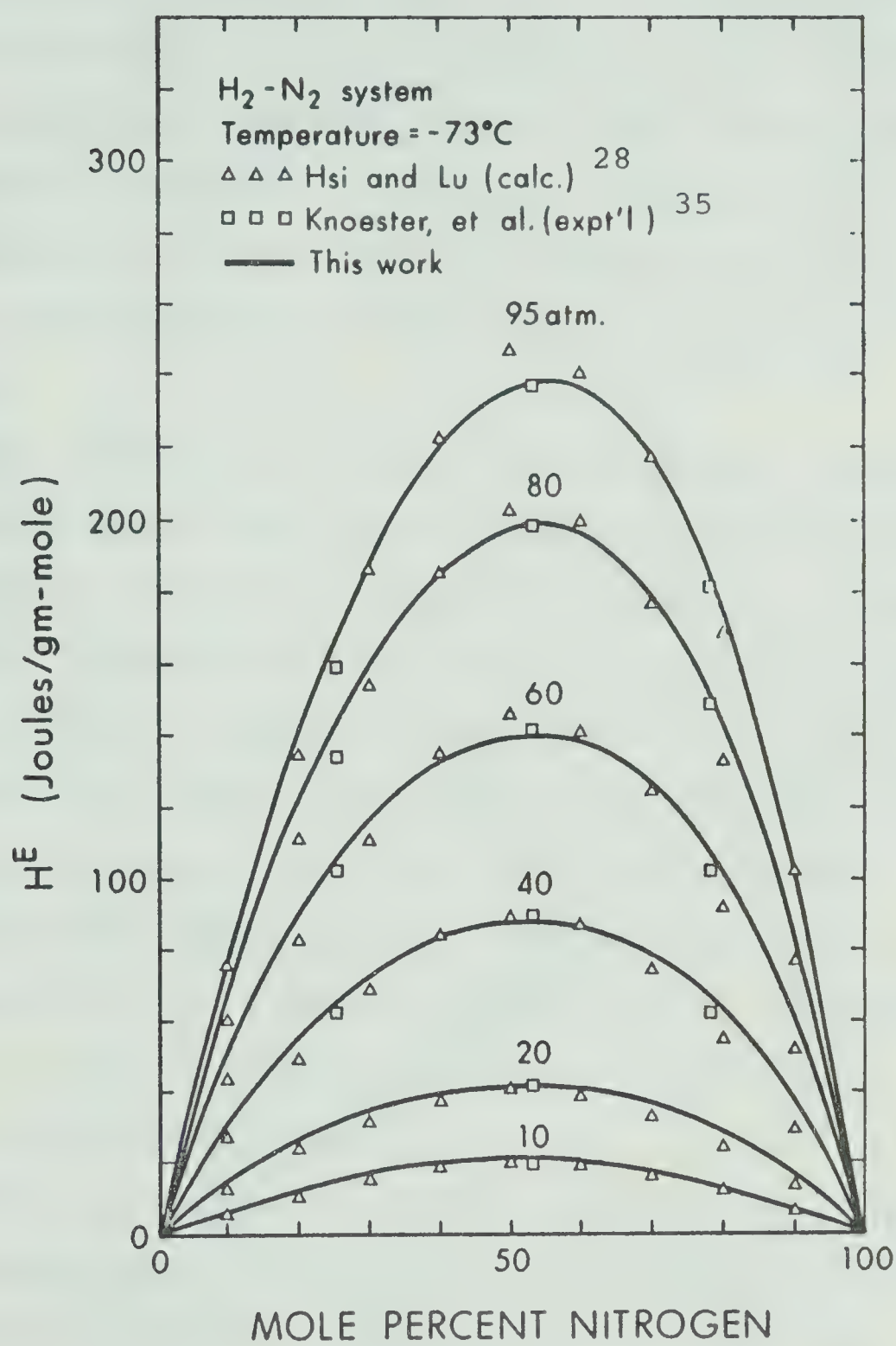


Figure 13. Comparison of the Excess Enthalpies for Hydrogen-Nitrogen System at -73°C

gases in the low density region, i.e., far removed from the critical state, the behaviour of the excess thermodynamic properties has been shown to obey binary collision theory completely². As shown in Equation (23) the excess enthalpy in the region of low density is linear in pressure and parabolic in mole fraction at constant temperature.

The behaviour of the heat of mixing as a function of pressure, for 50 mole percent nitrogen in the mixture with hydrogen at various temperatures studied, is shown in Figure 14. The excess enthalpies at temperatures of 7, -3, and -73°C are shown by a linear function of pressure up to 110 atm., while at 20°C the linearity is excellent up to 130 atm. Figure 15 shows comparisons with the virial equation (Equation (23)). The excess second virial coefficients, E , were obtained from Brewer⁷. The Equation (23) is in good agreement at 20°C, but the deviation increases at low temperatures.

Shown in Figure 13 are the isobars of the smoothed excess enthalpies as a function of composition at -73°C. As expressed in Equation (23), all those isobars are excellent parabolas.

The temperature dependence of the excess enthalpy is shown in Figures 16 and 17 for 50 and 80 mole percent nitrogen, respectively, at pressures of 20, 60, 80, and 120 atm. with the literature values.

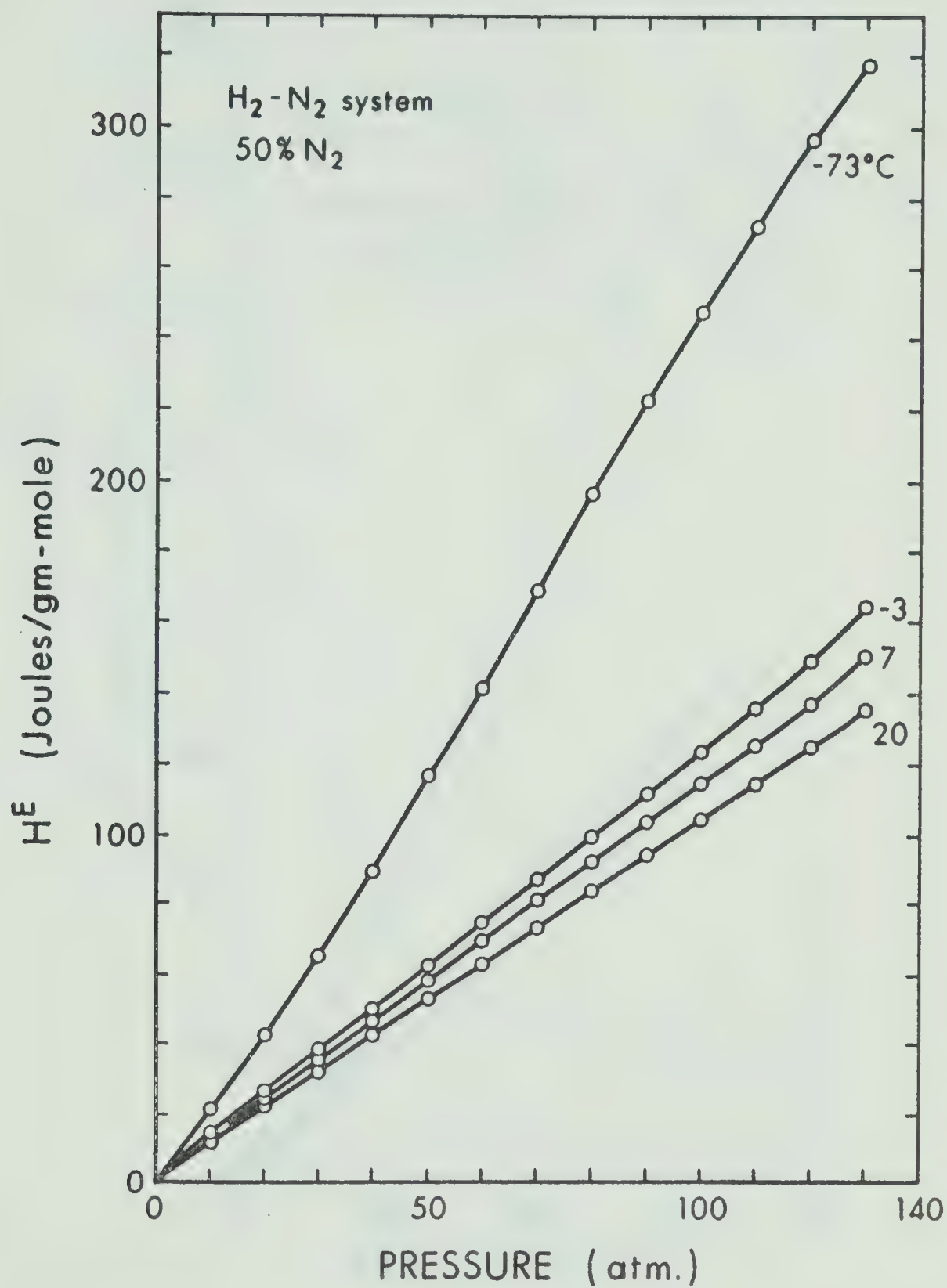


Figure 14. Isotherms of the Excess Enthalpies for 50 Mole Percent Nitrogen of Hydrogen-Nitrogen Mixture as a Function of Pressure

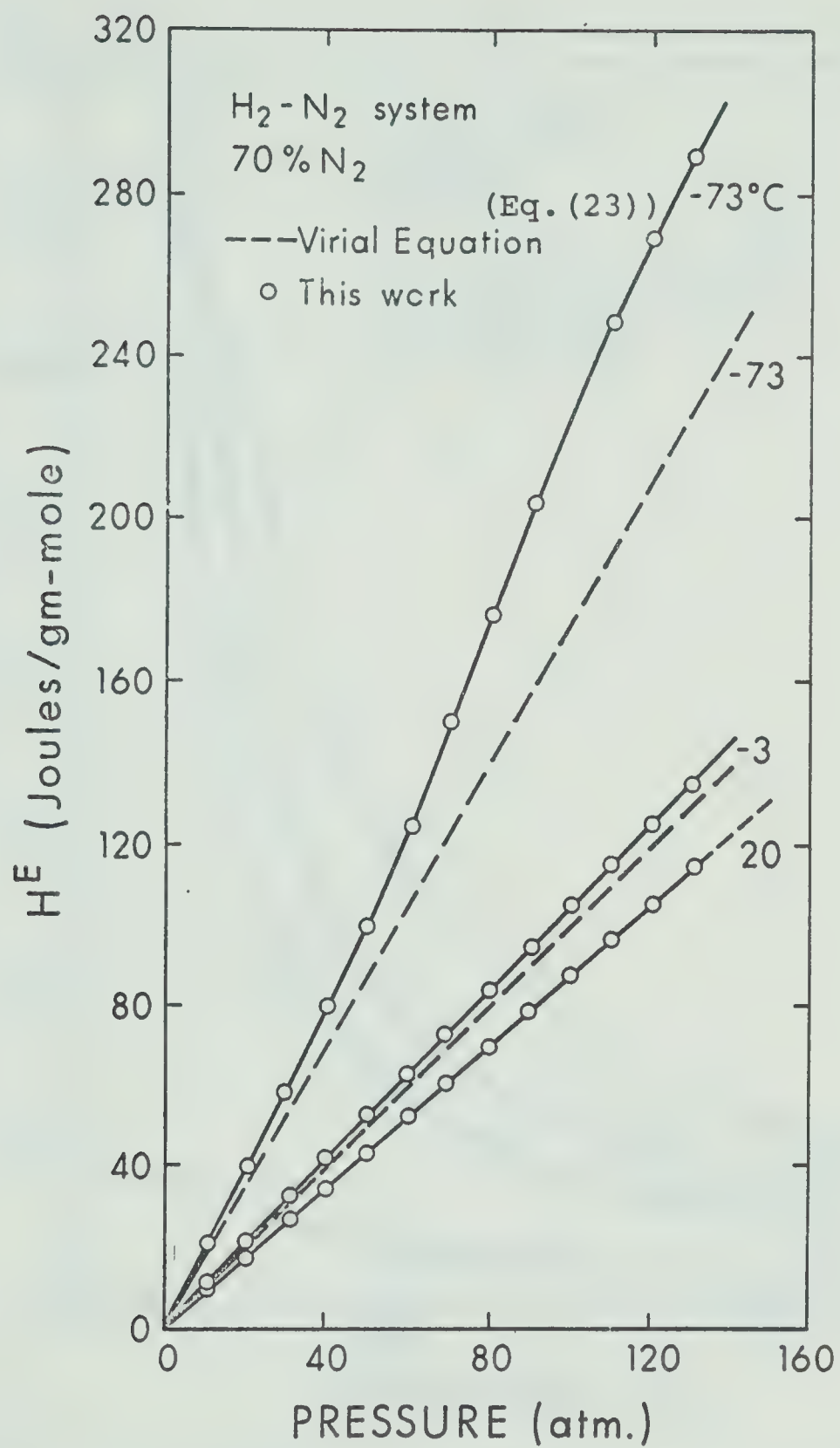


Figure 15. Comparison of the Excess Enthalpies with the Virial Equation of State for Hydrogen-Nitrogen System

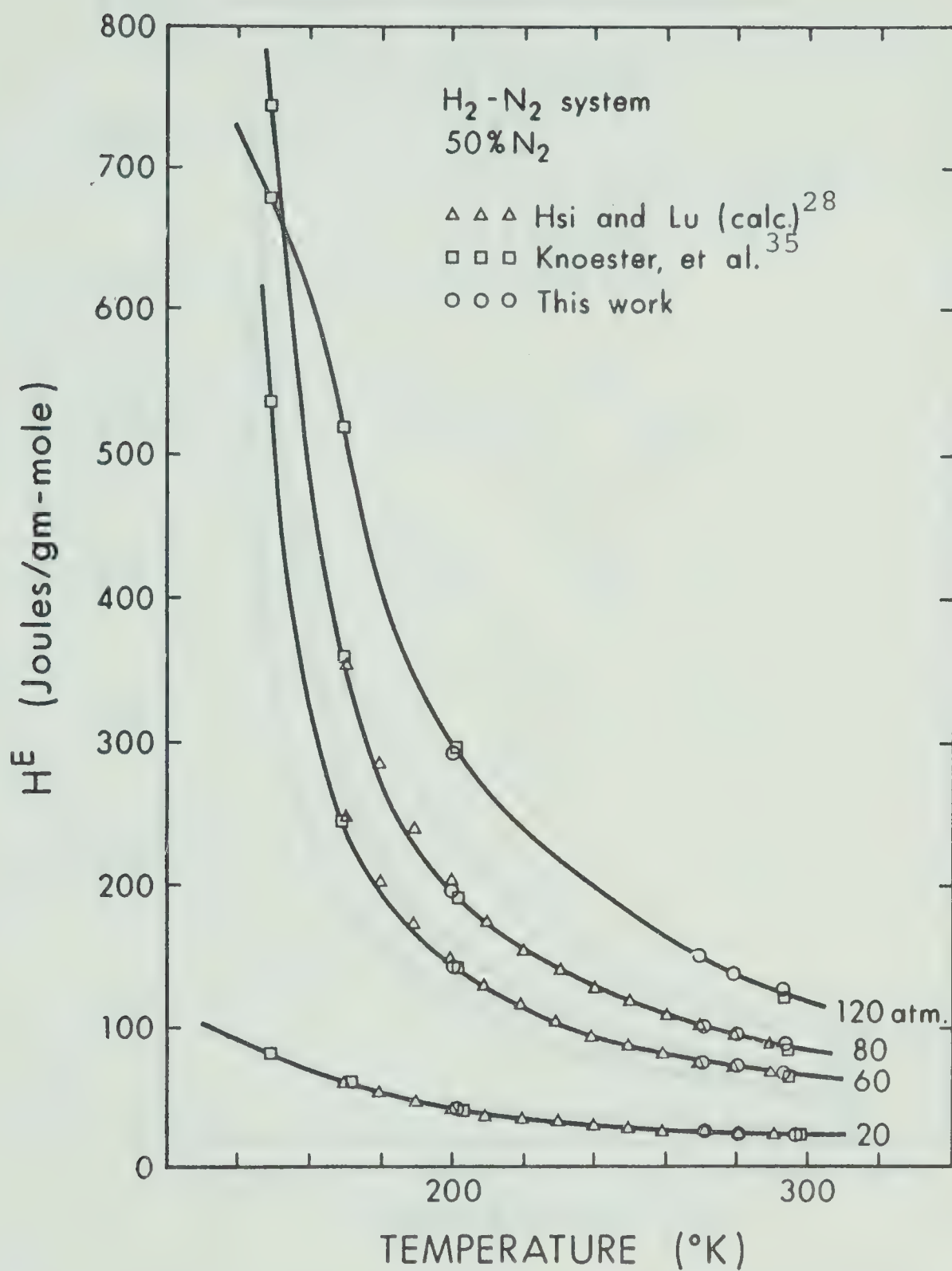


Figure 16. Isobars of the Excess Enthalpies for 50 Mole Percent Nitrogen of Hydrogen-Nitrogen Mixture as a Function of Temperature

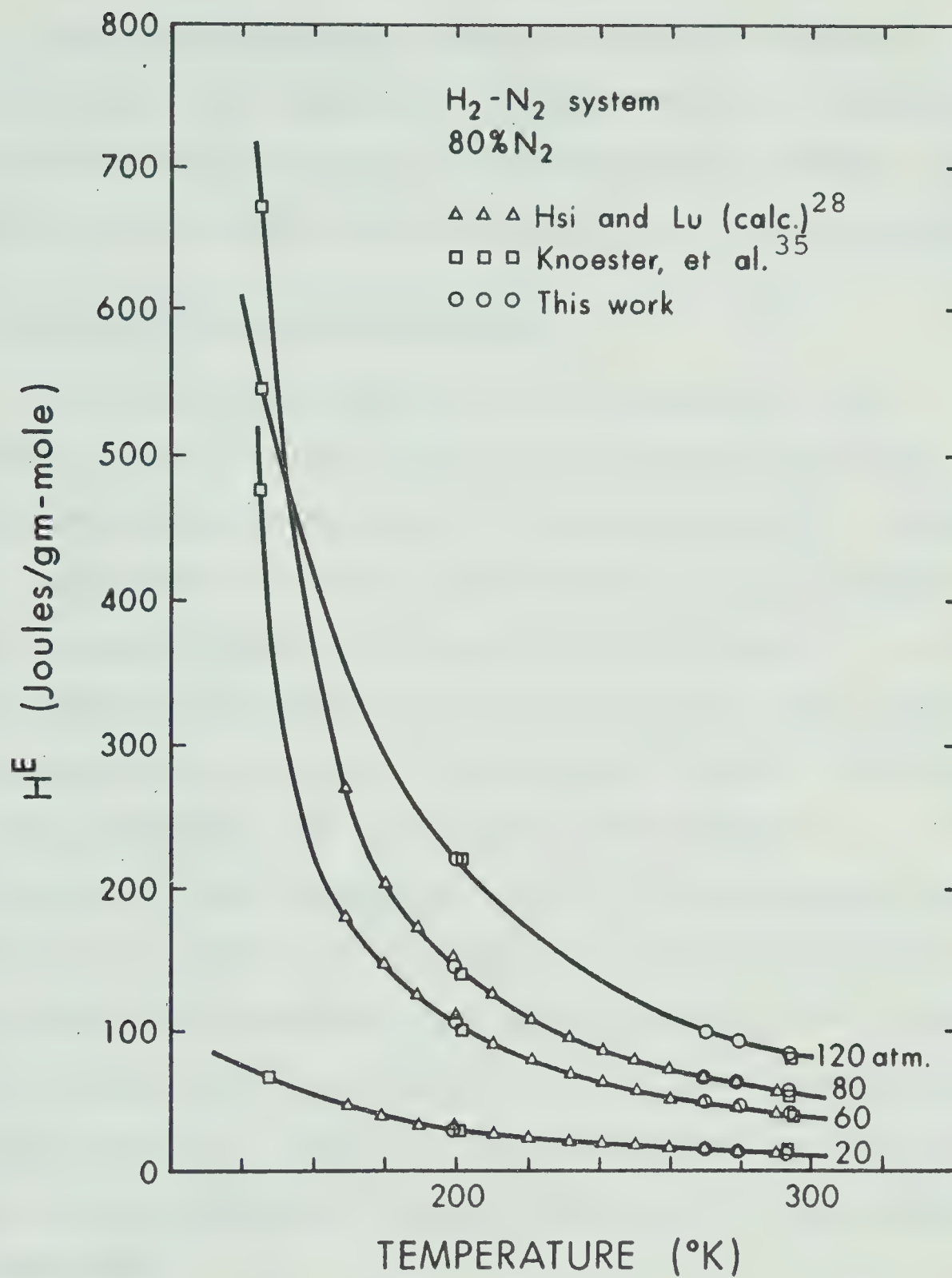


Figure 17. Isobars of the Excess Enthalpies for 80 Mole Percent Nitrogen of Hydrogen-Nitrogen Mixture as a Function of Temperature

The excess enthalpy increases when the critical point of one of the components in the mixture is approached. It is interesting to observe that the excess enthalpy has a maximum value at the vicinity of mixture critical locus.

B. Nitrogen-Carbon Dioxide System

The excess enthalpies of gaseous system at the vicinity of the critical point of one component of the mixture may be determined by the liquid theories⁵⁴. Also it is important to test the applicability of an equation of state and other empirical methods at that region. For this reason nitrogen-carbon dioxide system at 40°C was selected. That temperature is about 9°C above the critical temperature of carbon dioxide. The experiment was performed up to 130 atm. using the same equipment as that of hydrogen-nitrogen system. Some additional equipment was installed because of the particular behaviour of carbon dioxide, for instance, Joule -Thomson effect and extreme deviation of compressibility from ideality. The additional equipment and differences of the experimental method from the previous system are described.

Finally comparisons are made with the virial equation of state (Equation (23)), the B-W-R equation of state, and Scott's liquid theories, and the Yen and Alexander's generalized correlation.

1. Material Used

The nitrogen used for this system is the same as that of previous system as shown in Table III (high purity), and 99.9 percent pure carbon dioxide supplied by Canadian Liquid Air Co., Ltd. was used without further purification.

2. Experimental Work

The commercial carbon dioxide cylinder of 50 pounds in net weight is in two phases (liquid and gas) at a pressure of about 68 atm. To cover the high pressure range it was heated up to 55°C. The experimental method was essentially the same as that of hydrogen-nitrogen system except the composition determination.

Additional Installation

A 55°C water bath was constructed for the high pressure carbon dioxide supply. For the random mixing of water in the above bath a water pump was used.

When carbon dioxide or a mixture containing it passed through the regulating valve the Joule-Thomson effect was marked. To prevent the regulating valve and line after the regulating valve from freezing due to the carbon dioxide behaviour, another 60°C water bath was installed between the operating bath (it was also called a low temperature bath) and the regulating valve. Also a 6-foot-long heating tape wrapped the regulating valve and the copper tubing of the part just before the regulating valve and then the room

temperature bath of the previous system moved to between the regulating valve and the flowmeter. Since the compressibility of carbon dioxide changes strongly with pressure even at a constant temperature, the composition determination method used for the previous system was not suitable for this system. A gas chromatograph was used to determine the composition.

Temperature Level

The temperature studied was 40°C and it was controlled within 0.02°C during the experiment.

Composition Preparation

The commercial nitrogen gas cylinders were combined with one 50 pounds carbon dioxide cylinder to obtain various compositions. Figure 18 shows the combinations and the composition variations with pressure for various combinations. The compositions were determined by a continuous analyzing method with a calibrated gas chromatograph whose calibration data are given in Table XIV, Appendix B.

3. Reproducibility of Data and Data Smoothing

The experimental data of this system were collected as a function of pressure and at the same time the composition variation was observed by a continuous analysing method as a function of pressure. Then both data were matched to obtain the smoothed excess enthalpy data. The smoothing technique was the same as that used for the hydrogen-nitrogen system.

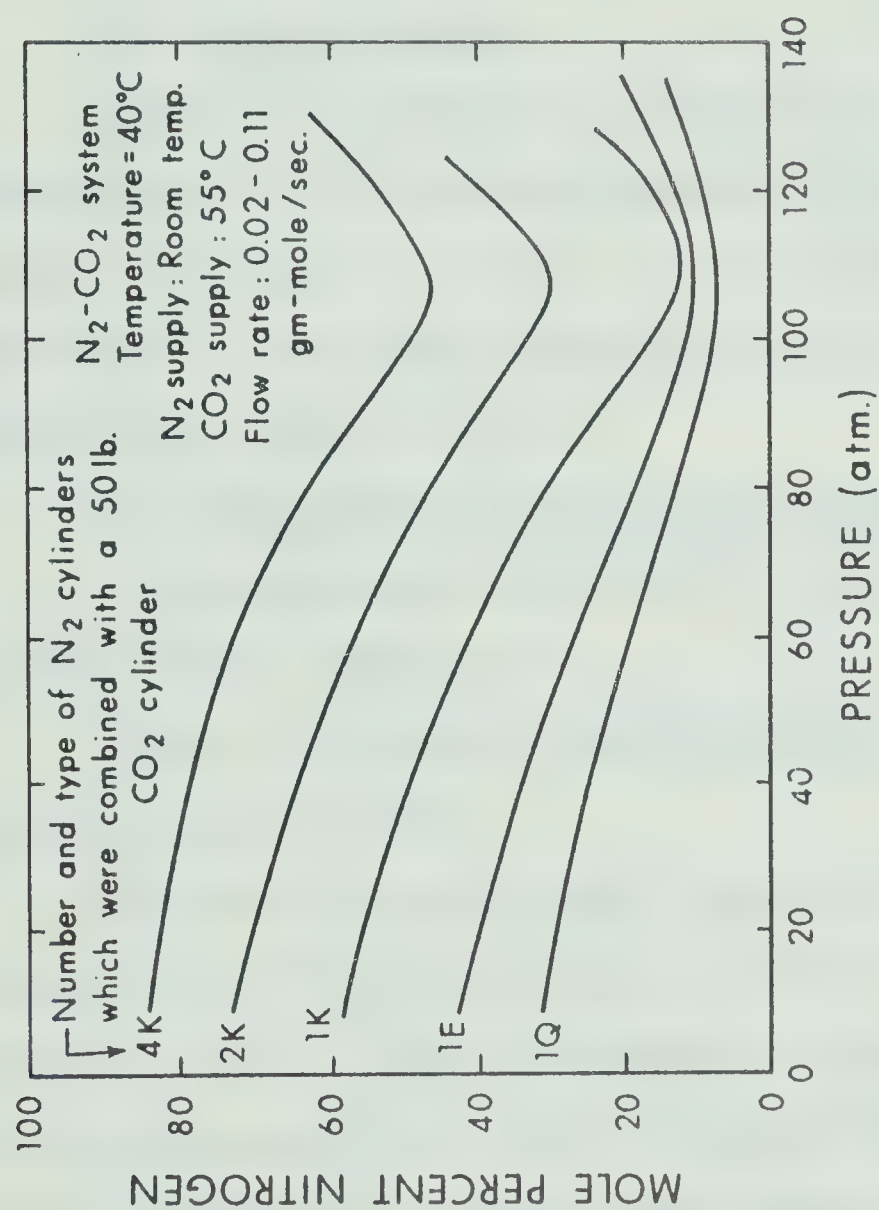


Figure 18. Composition Variations of Nitrogen-Carbon Dioxide System

The reproducibility of data was checked as follows. The data were collected for two different conditions of the carbon dioxide supply, one at 55°C and the other at 40°C. After smoothing both results, they were compared and were within 0.5 percent of each other.

4. Error Analysis

Errors introduced in the calculation of the excess enthalpy are from the same sources as hydrogen-nitrogen system, and they are almost the same magnitude. Therefore the error in the excess enthalpy data for this system is assumed less than 4 percent.

5. Experimental Results and Comparisons

The experimental raw data of this system are listed in Table XVIII, Appendix D.

Table VI shows the smoothed data of nitrogen-carbon dioxide system at 40°C.

Figures 19 and 20 show isobars of the excess enthalpies at 40°C and comparison with the results of Hejmadi, et al.²⁰ The agreement is within 3 percent. At low pressures the isobars are good symmetric parabolas. For the increased pressures they deviate to the carbon dioxide side because the enthalpy change of carbon dioxide with pressure is a stronger function than that of nitrogen.

The pressure dependence of the excess enthalpies for 10, 30, 50, 70, and 90 mole percent of nitrogen at

Table VI

Smoothed Excess Enthalpies of Nitrogen-Carbon Dioxide System

(Unit: Joules/gm-mole)

Pressure (atm.)	(0.1)	(0.2)	(0.3)	(0.4)	(0.5)	(0.6)	(0.7)	(0.8)	(0.9)
10.0	15.0	26.7	35.9	41.1	42.8	40.1	33.3	25.4	15.0
20.0	36.8	64.1	82.4	92.1	96.0	90.1	77.1	56.1	30.0
30.0	66.5	116.1	149.8	162.2	162.7	150.2	123.5	92.1	45.1
34.0	86.8	145.3	181.7	197.5	195.0	177.0	148.9	108.9	58.7
40.0	109.6	186.9	234.8	256.3	254.5	232.3	189.2	133.5	69.1
50.0	169.0	297.0	354.8	385.5	365.0	320.4	273.8	203.6	112.6
60.0	277.1	460.6	552.0	576.7	544.4	480.6	399.5	288.4	160.0
64.6	363.8	569.2	667.8	698.6	660.3	582.1	464.1	336.3	179.5
70.0	491.5	747.6	858.6	862.1	817.7	714.9	570.4	392.5	197.1
80.0	1021.3	1292.3	1415.8	1369.7	1243.3	1097.4	(904.2)	(667.5)	(363.5)*
90.0	2348.6	2763.5	2822.9	2604.3	2318.6	2009.6	(1679.5)	(1261.6)	(699.5)
100.0	2891.2	3417.7	3478.2	3204.1	2816.1	(2423.1)	(1997.6)	(1468.5)	(818.5)
110.0	2403.8	3340.9	3430.9	3249.1	2879.7	(2423.1)	(1860.0)	(1262.9)	(648.5)
120.0	1883.4	2939.8	3290.7	3244.1	2878.7	2391.1	(1787.3)	(1137.5)	(540.7)

* The figures in the bracket are extrapolated values.

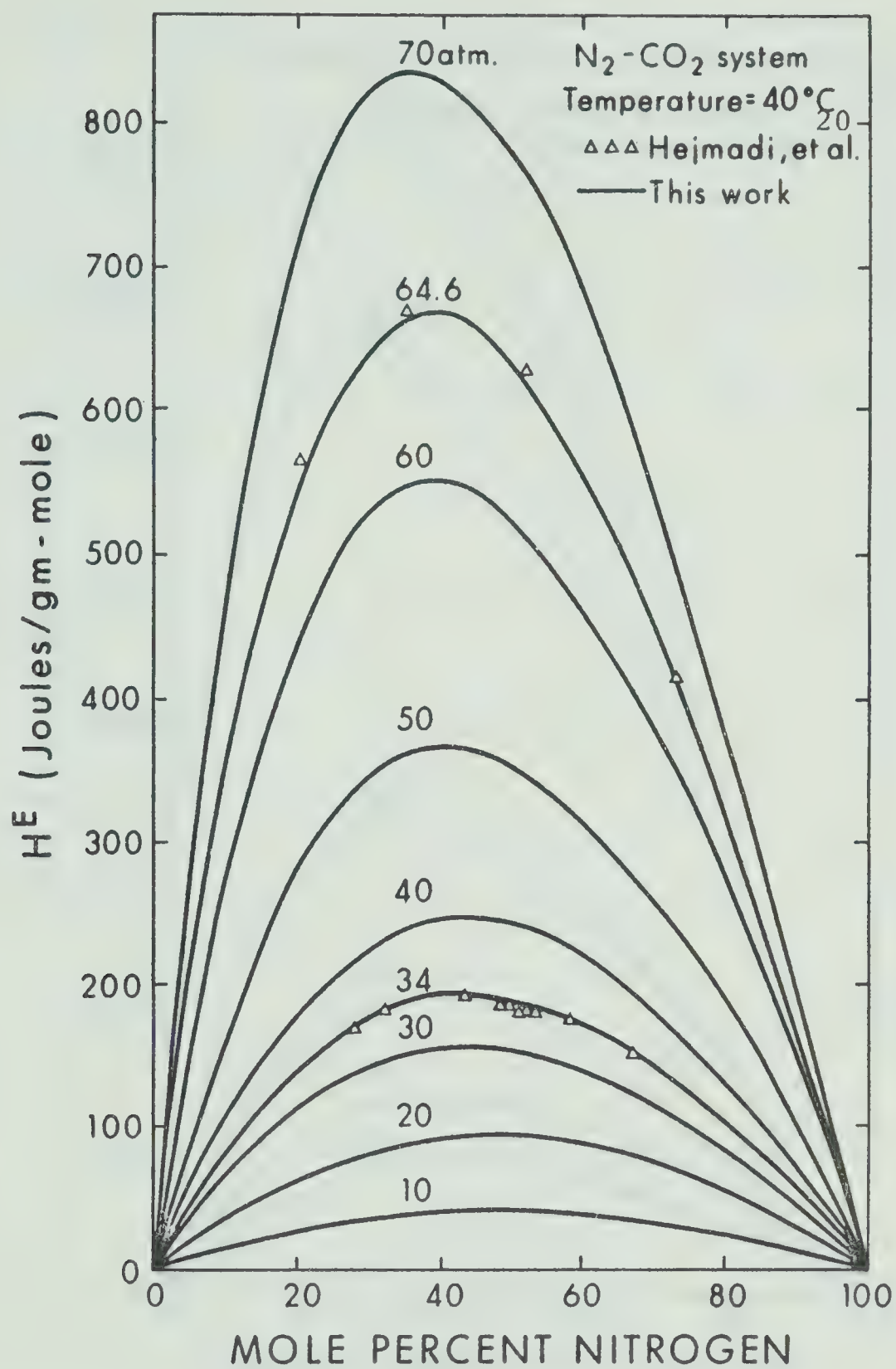


Figure 19. Isobars of the Excess Enthalpies of Nitrogen-Carbon Dioxide System at Low Pressures

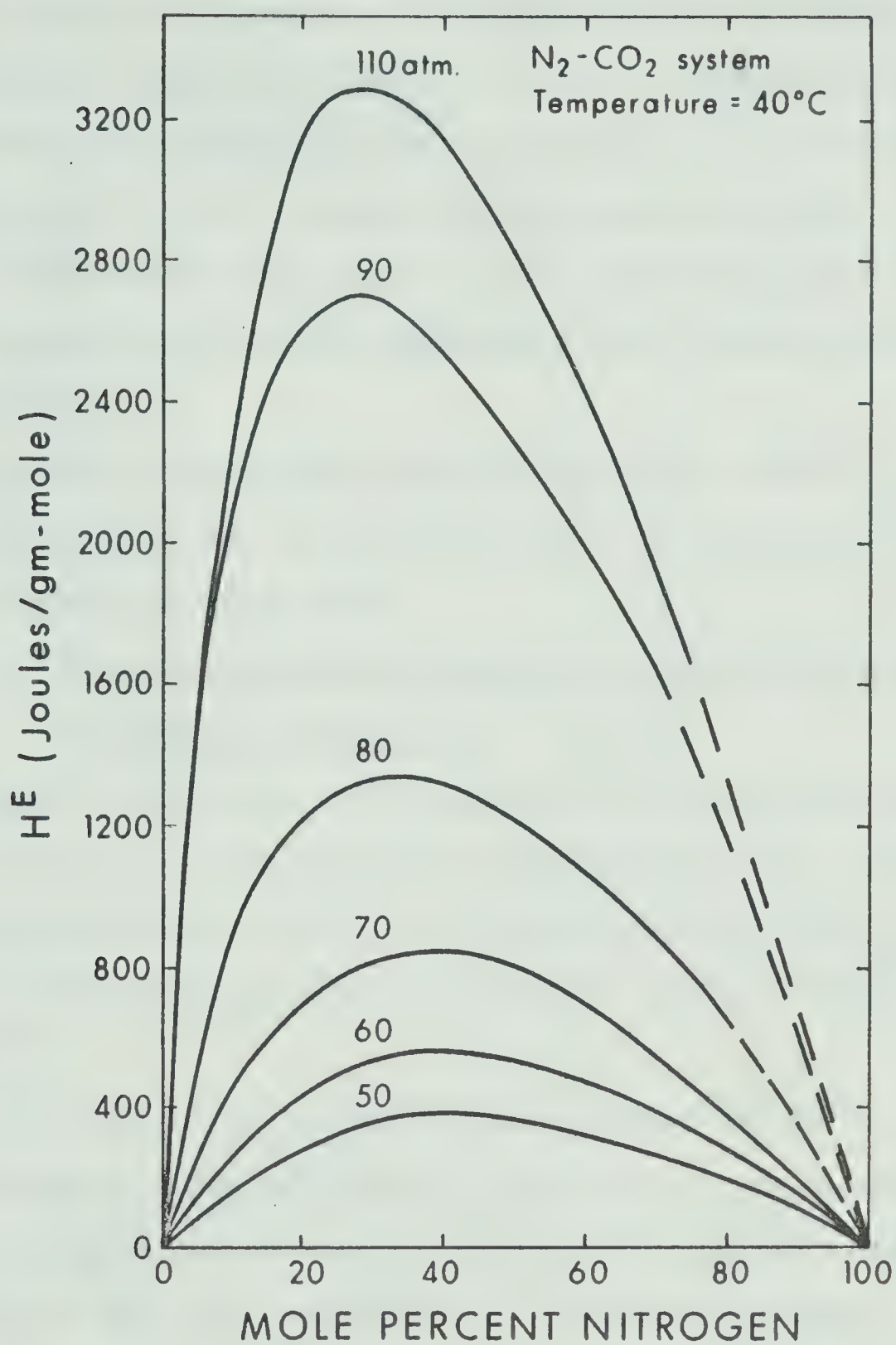


Figure 20. Isobars of the Excess Enthalpies of Nitrogen-Carbon Dioxide System at High Pressures

40°C is shown in Figure 21. At sufficiently low densities they are linear (Eq. (23)). It is obvious that the excess enthalpy variation with pressure is in its maximum at around 80 atm. because the enthalpy change of carbon dioxide with pressure at 40°C is maximum value while nitrogen is changing constantly with pressure at same temperature.

Figure 22 shows the excess enthalpies vanish at high temperatures but increase when the critical point of carbon dioxide is approached.

6. Data Interpretation and Comparisons with the Empirical Correlations

The behaviour of excess enthalpy for gaseous system at the vicinity of the critical temperature of one component of the mixture, can be explained by considering the pressure dependence of the enthalpy for nearly critical gases^{35,55}.

For the nitrogen-carbon dioxide system at 40°C, carbon dioxide exhibits critical behaviour. The energy due to the N₂-N₂ and N₂-CO₂ interactions is small compared with that of CO₂-CO₂ interaction. The first of these interactions can be neglected and we can consider the mixing of nitrogen and carbon dioxide to its partial pressure.

The enthalpy before mixing is then:

$$x H_{\text{CO}_2} (P, T) \quad (40)$$

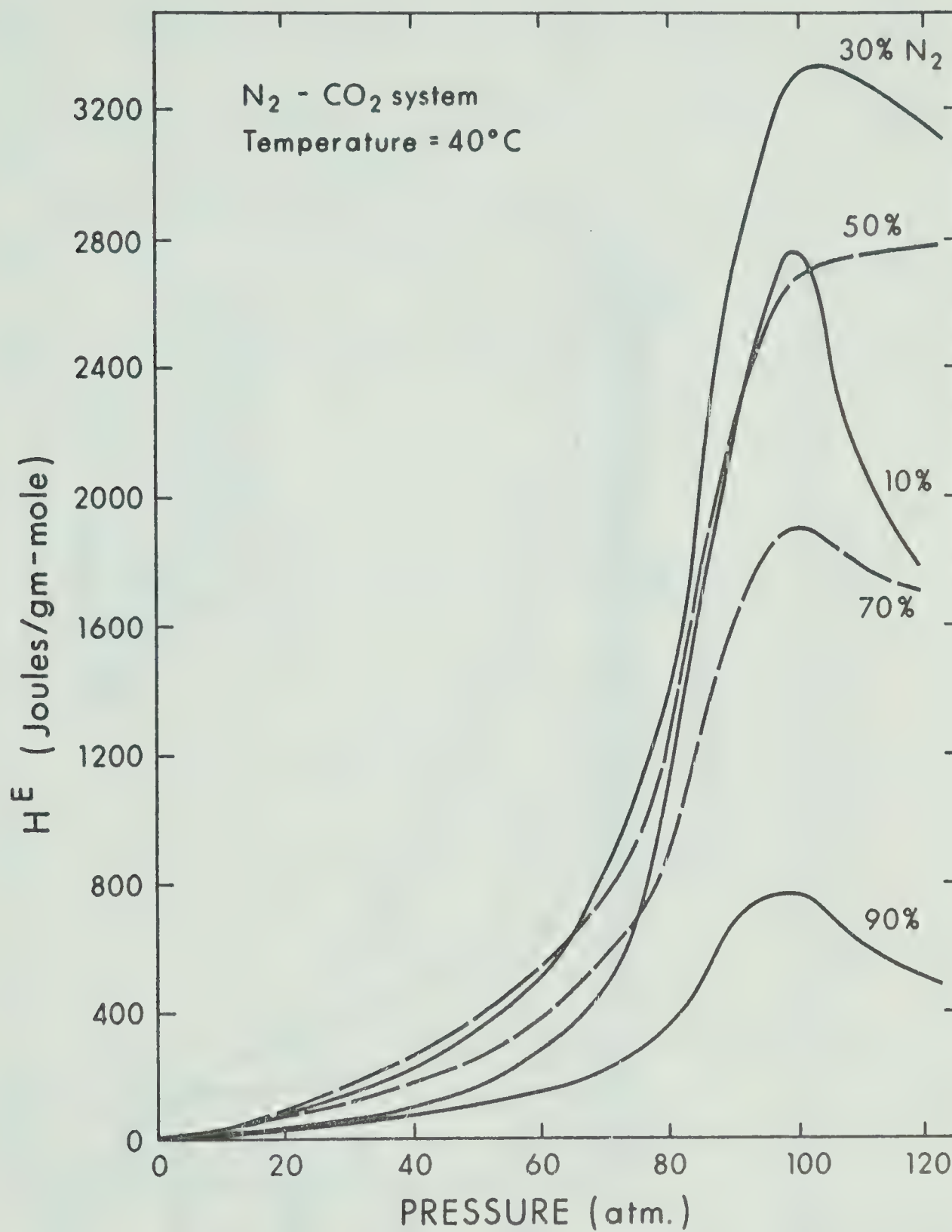


Figure 21. Pressure Dependence of the Excess Enthalpies of Nitrogen-Carbon Dioxide System

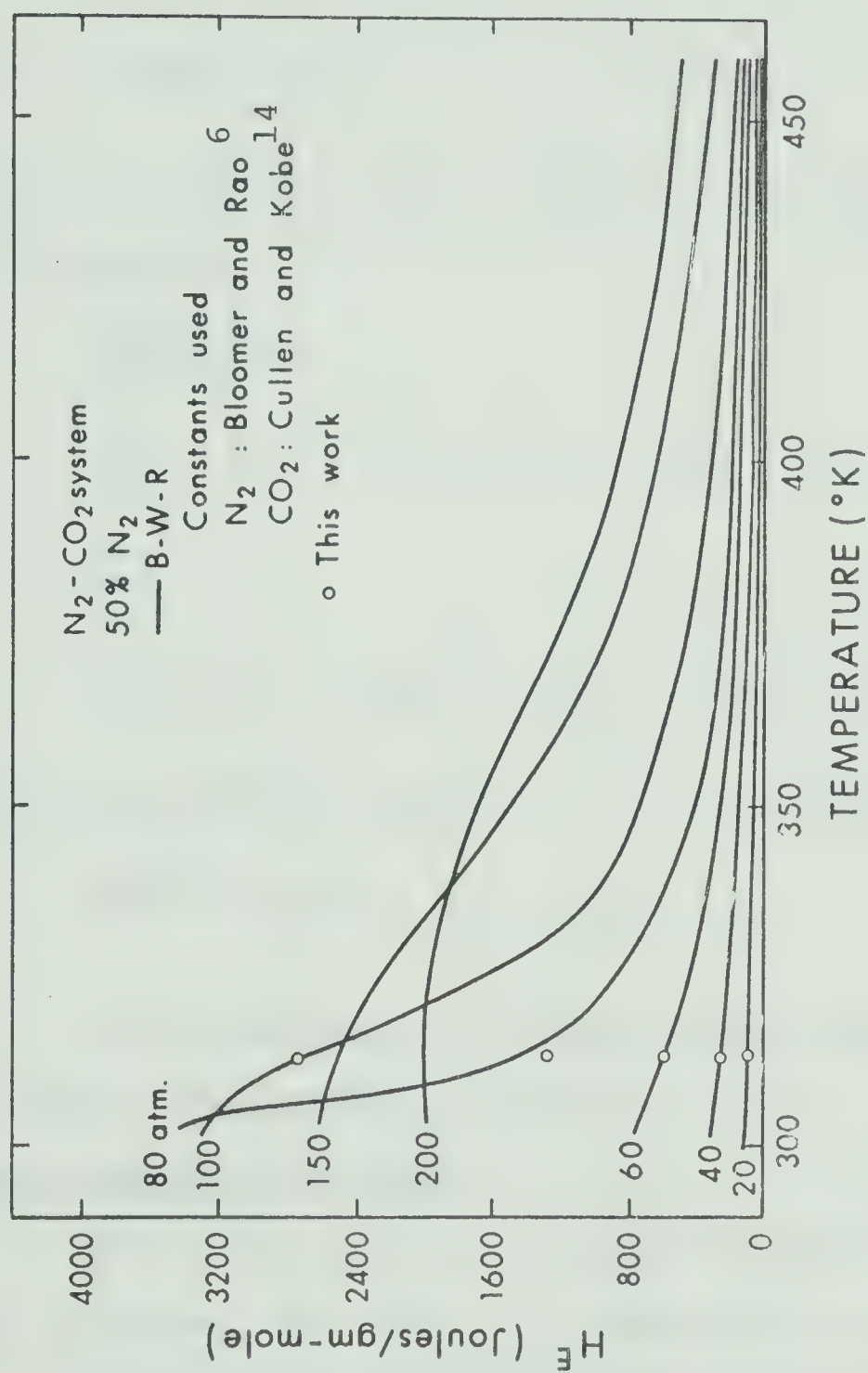


Figure 22. Temperature Dependence of the Excess Enthalpies of Nitrogen-Carbon Dioxide System

where x is the mole fraction of carbon dioxide. After mixing, the enthalpy is determined by the partial pressure of the carbon dioxide:

$$x H_{\text{CO}_2}(p, T) \quad (41)$$

where p denotes the partial pressure of carbon dioxide in the mixture.

Therefore,

$$H^E(x, P, T) = x[H_{\text{CO}_2}(p, T) - H_{\text{CO}_2}(P, T)] \quad (42)$$

or,

$$H^E(x, P, T) = x[H_{\text{CO}_2}^{\text{res}}(p, T) - H_{\text{CO}_2}^{\text{res}}(P, T)] \quad (43)$$

where the residual enthalpy, H^{res} , is defined as:

$$H^{\text{res}} = H(P, T) - H(P=0, T) \quad (44)$$

This expression is in qualitative agreement for nitrogen-carbon dioxide system at 40°C.

Virial Equation of State

The virial equation of state truncated after second term is linear (Eq. (23)). A comparison is made for 50 mole percent nitrogen with Equation (23) in Figure 23. To calculate the excess second virial coefficient, E , in Equation (23), B_{N_2} , B_{CO_2} , and $B_{\text{N}_2\text{-CO}_2}$ were obtained from Dymond and Smith¹⁷, Huff and Reed²⁹, and Cottrell, et al.¹²

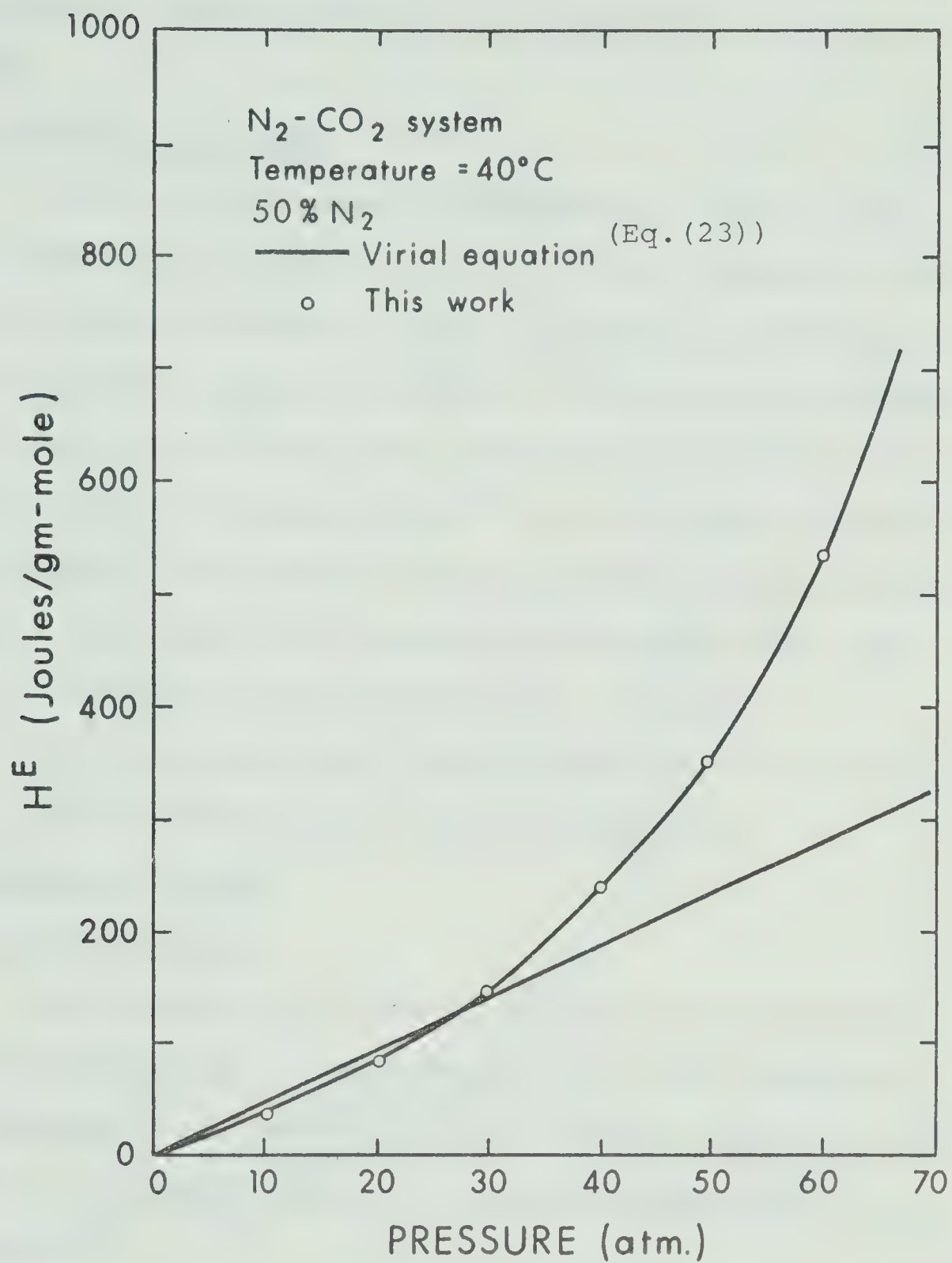


Figure 23. Comparison of the Excess Enthalpies of Nitrogen-Carbon Dioxide System with the Virial Equation of State

respectively. This equation is in agreement only up to 30 atm.

B-W-R Equation of State

Of the large number of equations of state, the B-W-R equation of state is one of the best equations for the high density region of gaseous systems. The comparisons are made in Figure 24 and 25. The constants of the B-W-R equation of state were from Cullen and Kobe¹⁴ for carbon dioxide, Bloomer and Rao⁶, and Crain and Sonntag¹³ for nitrogen. They were in good agreement in the entire range of the experiment except in the region where the excess enthalpies change rapidly with pressure.

The B-W-R equation, its constants, and the mixing rules for the mixture are listed in Appendix C.

Corresponding States

1) Liquid Theories

The behaviour of a binary mixture at high density can satisfactorily be explained by the liquid theories of Prigogine⁵⁰ and Scott⁵⁴. A more general survey of the theories on liquid mixtures is also available from Rowlinson⁵³.

Assuming that the mixture and its components obey the law of corresponding states, it is possible to form a reduced equation of state with variables reduced with parameters of the mixture. The excess enthalpy of a mixture was calculated by using data from reference gases

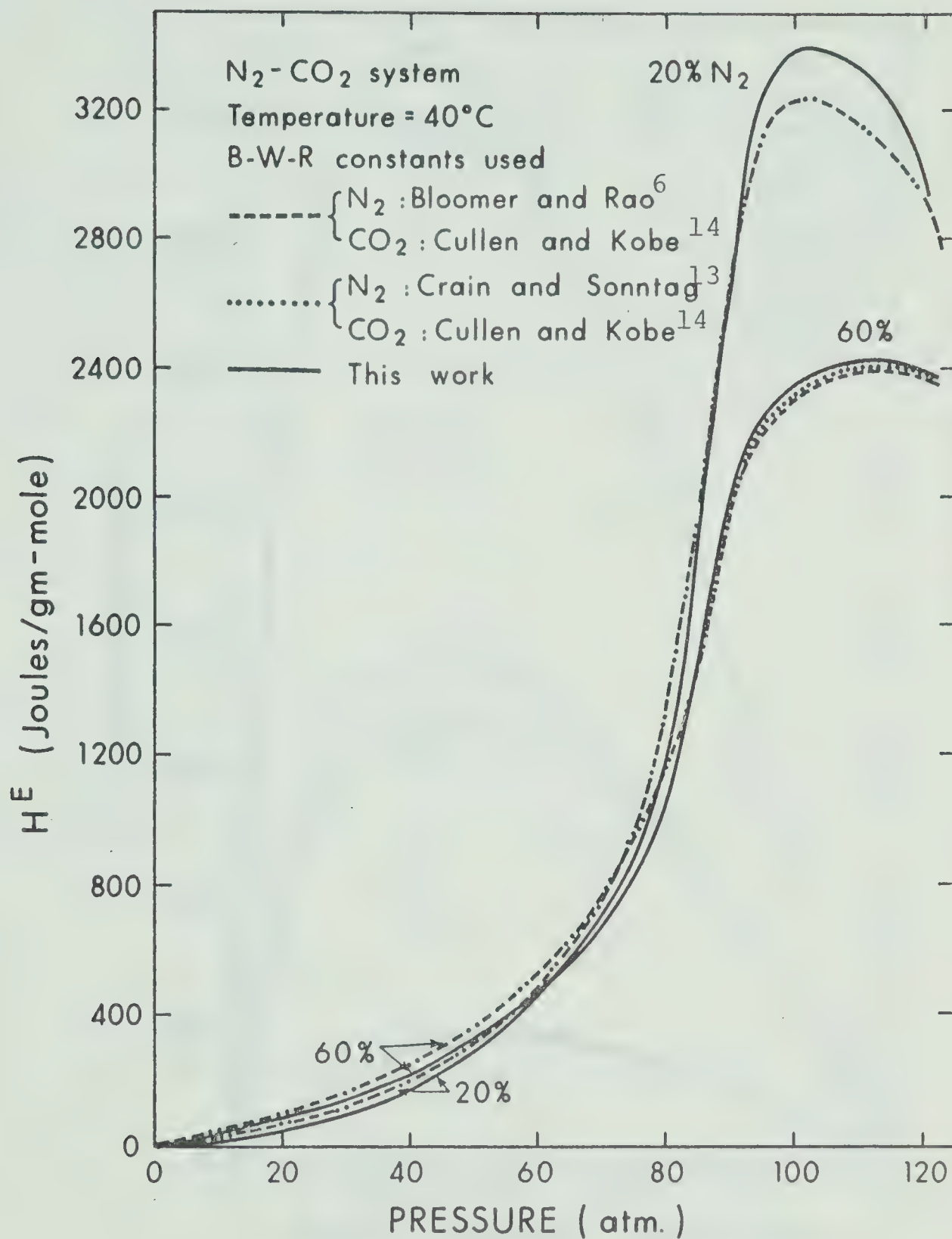


Figure 24. Comparison of the Excess Enthalpies of Nitrogen-Carbon Dioxide System with the B-W-R Equation of State as a Function of Pressure

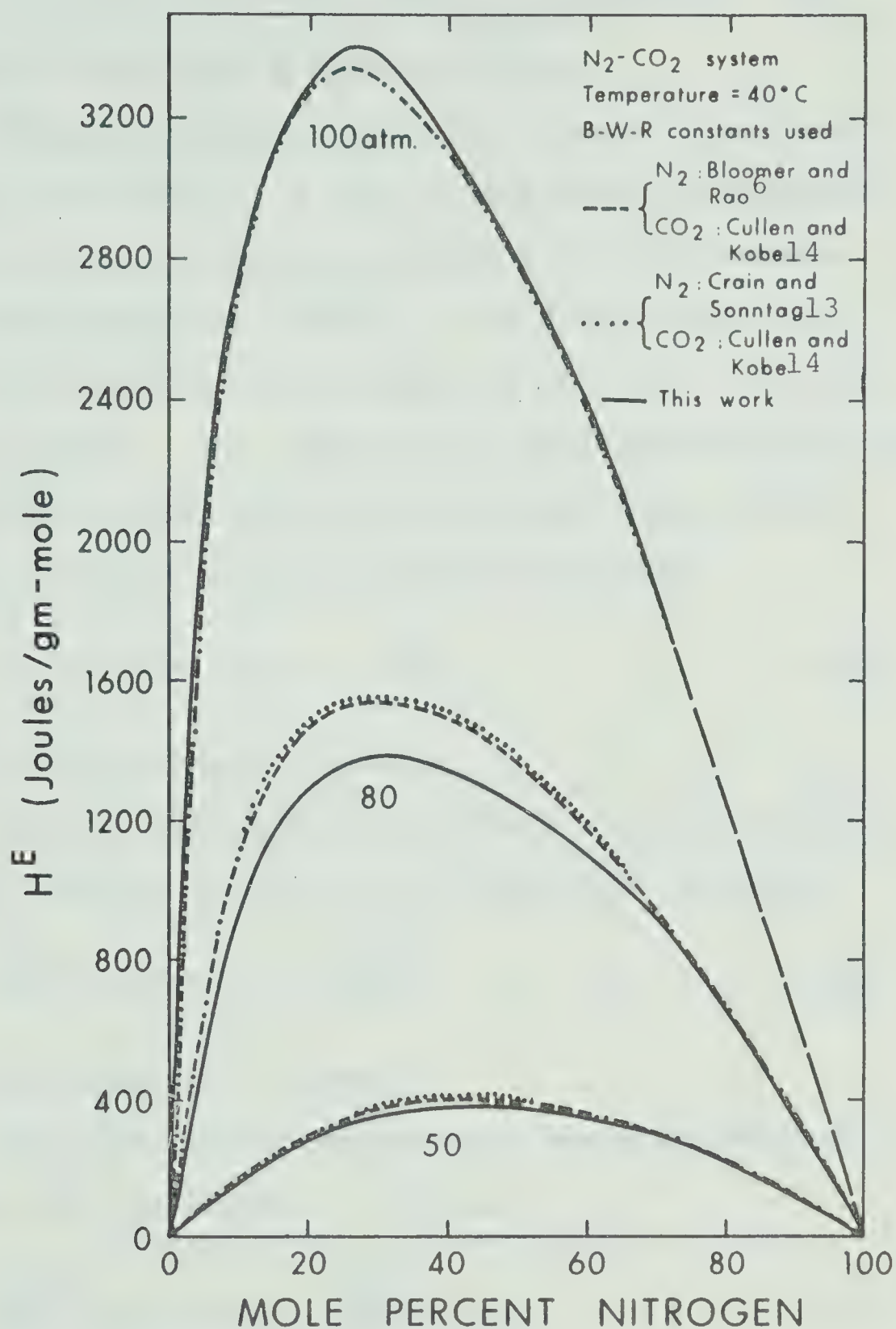


Figure 25. Comparison of the Excess Enthalpies of Nitrogen-Carbon Dioxide System with the B-W-R Equation of State as a Function of Composition

which was chosen one of the mixture components. The features of this theory are as follows.

The intermolecular potential energy is assumed to be of the form $\phi(r) = \epsilon f(\sigma/r)$ for each of the pairs present (A-A, A-B, and B-B), where r is the distance between the molecular centres, σ is a characteristic length for each kind of interacting pair and ϵ a characteristic energy. The components A (A-A interaction) and B (B-B interaction) then conform to the same reduced equation of state with the reduced variables:

$$T^* = \frac{kT}{\epsilon}, \quad P^* = \frac{P\sigma^3}{\epsilon} \quad (45)$$

where k is Boltzmann's constant.

The the residual enthalpy for both pure components is the same function of P^* and T^* , therefore, we have:

$$H^{\text{res}*} (P^*, T^*) = \frac{H^{\text{res}}}{N\epsilon} \quad (46)$$

where N is Avogadro's number.

The same reduced equation of state is assumed to be valid for the mixture. That is:

$$H_m^{\text{res}*} (P^*, T^*) = \frac{H_m^{\text{res}}}{N\epsilon_m} \quad (47)$$

For the potential the well-known Lennard-Jones (6-12) potential is chosen:

$$\phi_{AB}(r) = 4 \epsilon_{AB} \left[\left(\frac{\sigma_{AB}}{r} \right)^{12} - \left(\frac{\sigma_{AB}}{r} \right)^6 \right] \quad (48)$$

where parameters ϵ_{AB} and σ_{AB} are for the interaction of the molecules A and B of a mixture. For unlike pairs the usual combination rules are assumed:

$$\sigma_{AB} = \frac{1}{2} (\sigma_{AA} + \sigma_{BB}) \quad (49)$$

$$\epsilon_{AB} = (\epsilon_{AA} \epsilon_{BB})^{1/2}. \quad (50)$$

(a) Single Liquid Model

In liquids and dense gases each molecule has at every moment a number of neighbours. When assuming additivity of forces, it seems reasonable to replace the sum of pair interaction by some average interaction depending on the mole fractions. In the single liquid model we take an average $\langle \phi(r) \rangle$ over all kinds of pairs in the system assuming a random mixing, which gives:

$$\langle \phi(r) \rangle = x_A^2 \phi_{AA}(r) + 2x_A x_B \phi_{AB}(r) + x_B^2 \phi_{BB}(r). \quad (51)$$

From Equations (48) and (51), one obtains:

$$\begin{aligned} \langle \phi(r) \rangle = & 4 \left[x_A^2 \epsilon_{AA} \left\{ \left(\frac{\sigma_{AA}}{r} \right)^{12} - \left(\frac{\sigma_{AA}}{r} \right)^6 \right\} \right. \\ & + 2x_A x_B \epsilon_{AB} \left\{ \left(\frac{\sigma_{AB}}{r} \right)^{12} - \left(\frac{\sigma_{AB}}{r} \right)^6 \right\} \\ & \left. + x_B^2 \epsilon_{BB} \left\{ \left(\frac{\sigma_{BB}}{r} \right)^{12} - \left(\frac{\sigma_{BB}}{r} \right)^6 \right\} \right] \quad (52) \end{aligned}$$

and also from Equation (48), we have:

$$\langle \phi(r) \rangle = 4 \langle \epsilon \rangle \left\{ \left(\frac{\langle \epsilon \rangle}{r} \right)^{12} - \left(\frac{\langle \sigma \rangle}{r} \right)^6 \right\} . \quad (53)$$

From Equations (52) and (53), we have:

$$\langle \epsilon \rangle = \frac{(x_A^2 \epsilon_{AA}^{\sigma_{AA}}{}^6 + 2x_A x_B \epsilon_{AB}^{\sigma_{AB}}{}^6 + x_B^2 \epsilon_{BB}^{\sigma_{BB}}{}^6)^2}{x_A^2 \epsilon_{AA}^{\sigma_{AA}}{}^{12} + 2x_A x_B \epsilon_{AB}^{\sigma_{AB}}{}^{12} + x_B^2 \epsilon_{BB}^{\sigma_{BB}}{}^{12}} \quad (54)$$

and

$$\langle \sigma \rangle = \left(\frac{x_A^2 \epsilon_{AA}^{\sigma_{AA}}{}^{12} + 2x_A x_B \epsilon_{AB}^{\sigma_{AB}}{}^{12} + x_B^2 \epsilon_{BB}^{\sigma_{BB}}{}^{12}}{x_A^2 \epsilon_{AA}^{\sigma_{AA}}{}^6 + 2x_A x_B \epsilon_{AB}^{\sigma_{AB}}{}^6 + x_B^2 \epsilon_{BB}^{\sigma_{BB}}{}^6} \right)^{1/6} . \quad (55)$$

Now choosing one of the two components in the mixture as a reference gas (denoted by subscript R), from Equation (45) the reduced variables are:

$$\left. \begin{aligned} P^* &= \frac{\langle \sigma \rangle^3}{\langle \epsilon \rangle} P_m = \frac{\sigma_R^3}{\epsilon_R} P_R \\ T^* &= \frac{k}{\langle \epsilon \rangle} T_m = \frac{k}{\epsilon_R} T_R \end{aligned} \right\} \quad (56)$$

and from Equations (46), (47), and (56):

$$\frac{H_m^{\text{res}}}{N \langle \epsilon \rangle} \left(\frac{\langle \sigma \rangle^3}{\langle \epsilon \rangle} P_m, \frac{k}{\langle \epsilon \rangle} T_m \right) = \frac{H_R^{\text{res}}}{N \epsilon_R} \left(\frac{\sigma_R^3}{\epsilon_R} P_R, \frac{k}{\epsilon_R} T_R \right) . \quad (57)$$

Converting to the normal units one has:

$$H_m^{\text{res}}(x, P_m, T_m) = \frac{\langle \varepsilon \rangle}{\varepsilon_R} H_R^{\text{res}}(P_R, T_R) \quad (58)$$

or

$$H_m^{\text{res}}(x, P_m, T_m) = \frac{\langle \varepsilon \rangle}{\varepsilon_R} H_R^{\text{res}}\left(\frac{\varepsilon_R}{\langle \varepsilon \rangle} \frac{\langle \sigma \rangle^3}{\sigma_R^3} P_m, \frac{\varepsilon_R}{\langle \varepsilon \rangle} T_m\right) \quad (59)$$

from which H_m^{res} may be determined if H_R^{res} is known at the indicated conditions of pressure and temperature.

Then excess enthalpy is calculated from Equation (1).

(b) Two Liquid Model

Whereas in the foregoing model the molecular potentials were averaged over all the binary interactions, it seems obvious to apply also a model in which the interactions of A-molecules with neighbours are distinguished from those of B-molecules with surrounding particles. So in the two liquid model one considers the two average potentials $\langle \phi(r) \rangle_A$ and $\langle \phi(r) \rangle_B$. Under the same conditions as for the single liquid model, we have:

$$\langle \phi(r) \rangle_A = x_A \phi_{AA}(r) + x_B \phi_{AB}(r) \quad (60)$$

$$\langle \phi(r) \rangle_B = x_B \phi_{BB}(r) + x_A \phi_{AB}(r). \quad (61)$$

From Equation (48), (60), and (61), we have:

$$\langle \epsilon \rangle_A = \frac{(x_A^{\epsilon_{AA}\sigma_{AA}}{}^6 + x_B^{\epsilon_{AB}\sigma_{AB}}{}^6)^2}{x_A^{\epsilon_{AA}\sigma_{AA}}{}^{12} + x_B^{\epsilon_{AB}\sigma_{AB}}{}^{12}} \quad (62)$$

$$\langle \sigma \rangle_A = \left(\frac{x_A^{\epsilon_{AA}\sigma_{AA}}{}^{12} + x_B^{\epsilon_{AB}\sigma_{AB}}{}^{12}}{x_A^{\epsilon_{AA}\sigma_{AA}}{}^6 + x_B^{\epsilon_{AB}\sigma_{AB}}{}^6} \right)^{1/6} \quad (63)$$

and $\langle \epsilon \rangle_B$ and $\langle \sigma \rangle_B$ are similar. The thermodynamic properties of the mixture are assumed to be the molar averages of the corresponding properties of these two liquids. This model has an expansion of enthalpy of mixture as:

$$H_m^{\text{res}} = x_A \langle H^{\text{res}} \rangle_A + x_B \langle H^{\text{res}} \rangle_B \quad (64)$$

where

$$\langle H^{\text{res}} \rangle_A (P_m, T_m) = \frac{\langle \epsilon \rangle_A}{\epsilon_R} H_R^{\text{res}} \left(\frac{\epsilon_R}{\langle \epsilon \rangle_A} \frac{\langle \sigma \rangle_A^3}{\sigma_R^3} P_m, \frac{\epsilon_R}{\langle \epsilon \rangle_A} T_m \right) \quad (65)$$

and similarly for $\langle H^{\text{res}} \rangle_B$.

Then the excess enthalpy is obtained from:

$$H^E = x_A \{ \langle H^{\text{res}} \rangle_A - H_A^{\text{res}} \} + x_B \{ \langle H^{\text{res}} \rangle_B - H_B^{\text{res}} \}. \quad (66)$$

(c) Three Liquid Model

Since in a binary mixture three kinds of binary interactions are present, it is interesting to consider also the mixture as a system of three fluids, each

characterized by one kind of pair interaction.

The residual enthalpy of a binary system is then expressed as:

$$H_m^{\text{res}} = x_A^2 H_A^{\text{res}} + 2x_A x_B H_{AB}^{\text{res}} + x_B^2 H_B^{\text{res}} \quad (67)$$

where H_{AB}^{res} is the residual enthalpy of a gas with the mixed interaction, characterized by the parameter ϵ_{AB} and σ_{AB} as:

$$H_{AB}^{\text{res}}(P_m, T_m) = \frac{\epsilon_{AB}}{\epsilon_R} H_R^{\text{res}} \left(\frac{\epsilon_R}{\epsilon_{AB}} \frac{\sigma_{AB}^3}{\sigma_R^3} P_m, \frac{\epsilon_R}{\epsilon_{AB}} T_m \right). \quad (68)$$

The the excess enthalpy for this model is expressed as:

$$H^E = 2x_A x_B \left\{ H_{AB}^{\text{res}} - \frac{1}{2} (H_A^{\text{res}} + H_B^{\text{res}}) \right\}. \quad (69)$$

This expression shows that the mole fraction dependence of the excess enthalpy calculated with the three liquid model is parabolic.

Comparisons are made in Figure 26 and Table VII. The two liquid model is in good agreement for this system when nitrogen is chosen as a reference gas. The enthalpy data for pure gases were taken from Hilsenrath, et al.²², Din¹⁶, and Newitt, et al.⁴⁵ In the case of choice of carbon dioxide as a reference gas, since even

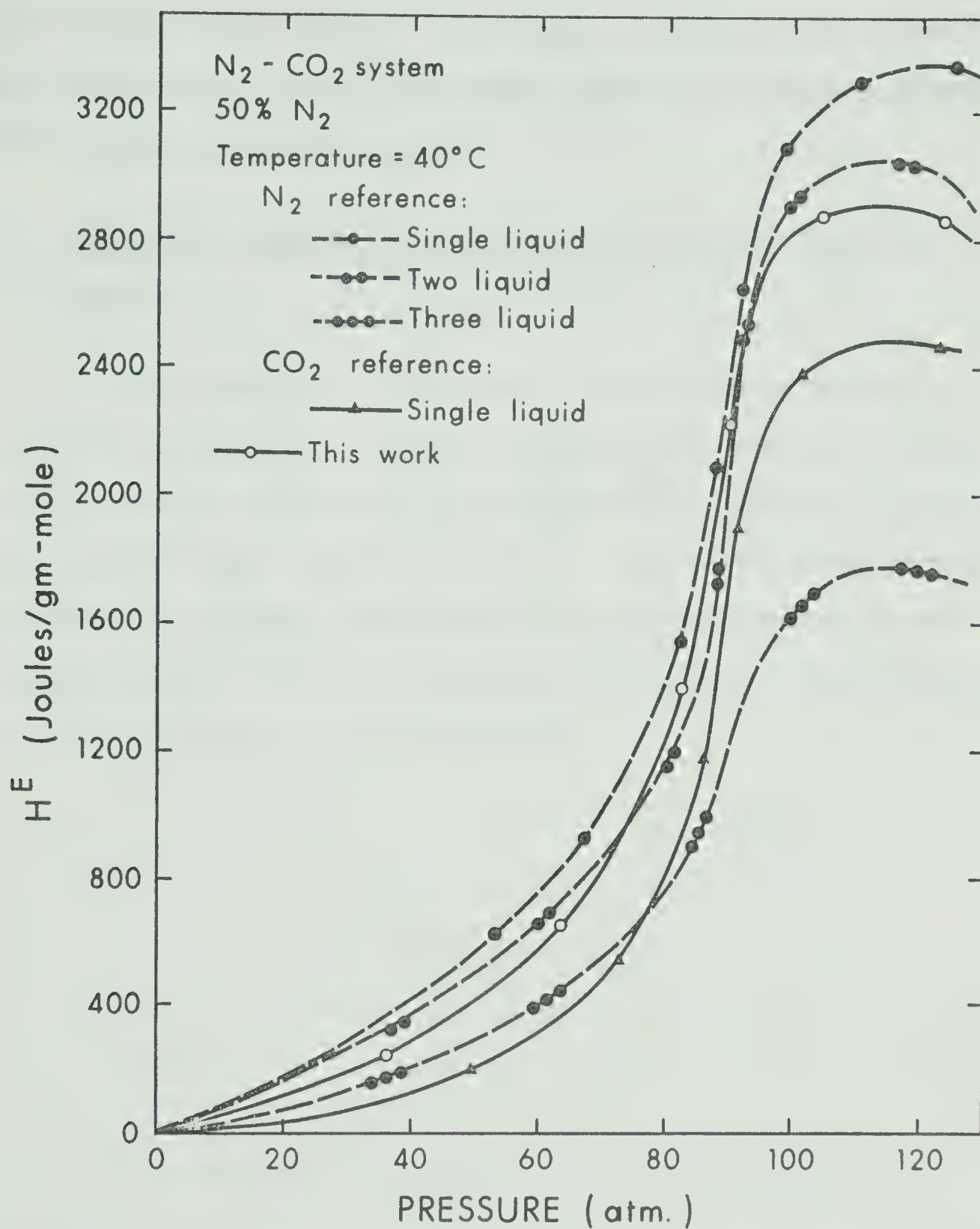


Figure 26. Comparison of the Excess Enthalpies of Nitrogen-Carbon Dioxide System with the Liquid Theories

the single liquid model the excess enthalpies calculated are relatively small, it is not suitable to choose carbon dioxide as a reference gas.

2) Yen and Alexander's Generalized Enthalpy Departure Chart

The generalized approach for the thermodynamic properties prediction from the empirical data was suggested by Lydersen, Greenkorn, and Hougen³⁶. Recently, Yen and Alexander⁶⁰ modified this method. Table VII shows comparisons of the excess enthalpies of nitrogen-carbon dioxide system at 40°C with other prediction method. This method is only in qualitative agreement.

Table VII

Comparisons of the Excess Enthalpies of Nitrogen-Carbon
Dioxide System with Calculations at 40°C for 50 Mole

Percent Nitrogen

Pressure (atm)	<u>Excess Enthalpies (Joules/gm-mole)</u>						
	<u>This work</u>	<u>B-W-R^a</u>	<u>B-W-R^b</u>	<u>Y&A⁶⁰</u>	<u>1-Liq.^c</u>	<u>2-Liq.^d</u>	<u>1-Liq.^e</u>
70	818	863	876	1131	1019	890	451
80	1243	1381	1395	1930	1444	1312	833
90	2318	2347	2361	2242	2317	2148	1620
100	2816	2768	2783	2436	3158	2947	2432
110	2880	2827	2843	2577	3298	3009	2467
120	2879	2791	2808	2660	3346	3054	2442

Note: ^a Constant Used

Nitrogen: Bloomer and Rao⁶

Carbon Dioxide: Cullen and Kobe¹⁴

^b Constant Used

Nitrogen: Crain and Sonntag¹³

Carbon Dioxide: Cullen and Kobe¹⁴

^c Single Liquid Model for Nitrogen Reference

^d Two Liquid Model for Nitrogen Reference

^e Single Liquid Model for Carbon Dioxide Reference

Physical Constants Used in Calculation

<u>Material</u>	ϵ/k	σ	T_c	P_c	V_c	z_c
	<u>(°K)</u>	<u>(Å)</u>	<u>(°K)</u>	<u>(atm)</u>	<u>(l/g-mole)</u>	<u>(-)</u>
Nitrogen	95.05	3.698	126.2	33.5	0.0901	0.291
Carbon Dioxide	205	4.07	304.2	72.9	0.094	0.274

SUMMARY AND CONCLUSIONS

1. A flow-type isothermal calorimeter designed for the study of the enthalpy changes on mixing in a gaseous system was constructed and tested. The experiment carried out in the temperature range between -73 and $+60^{\circ}\text{C}$, and for the pressures up to 130 atm.
2. The hydrogen-nitrogen system was chosen to test the calorimeter. The excess enthalpy data of this system were in good agreement with the literature, within 5 percent.
3. A study has been done for the system of nitrogen-carbon dioxide at 40°C and up to 130 atm. for the entire composition range. The data for nitrogen-carbon dioxide system were compared with the virial equation of state, the B-W-R equation of state, the generalized method, and the liquid theories.
4. The agreement with the B-W-R equation of state is quite good for the entire pressure range except the region of rapid change of enthalpy of carbon dioxide with pressure, around 80 atm. The virial equation is limited to low densities, and the correlation of Yen and Alexander is in qualitative agreement. The two liquid theory is relatively in good agreement for nitrogen-carbon dioxide system, while the single and three liquid models deviate significantly.

5. To determine the mixture composition the calculation method may be used for the systems which are composed of materials whose compressibilities are in good linearity, and for which accurate P-V-T data are available. Otherwise the composition must be determined by direct analysis.

RECOMMENDATIONS FOR FUTURE WORK

1. An accurate automatic power supply is necessary to reduce experimental error and labour.
2. A mass flowmeter is preferred to the present gasometer system to decrease experimental error.
3. To obtain various compositions of a system, high pressure regulators are recommended.
4. The resistance of the heater in the calorimeter should be increased so that systems with large excess enthalpies can be studied without using excessive currents.
5. A device of gas separation and compression system is also recommended for the studies with expensive gases.
6. The vent system for the exhaust of the mixture should be improved particularly when toxic gases are used.
7. The tests for the virial equation of state including up to third term and for the Redlich-Kwong equation of state are recommended.
8. Studies on systems of polar and nonpolar gases at condition near the critical region should be made.

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APPENDIX A

CALORIMETER MIXING CHAMBER DRAWING

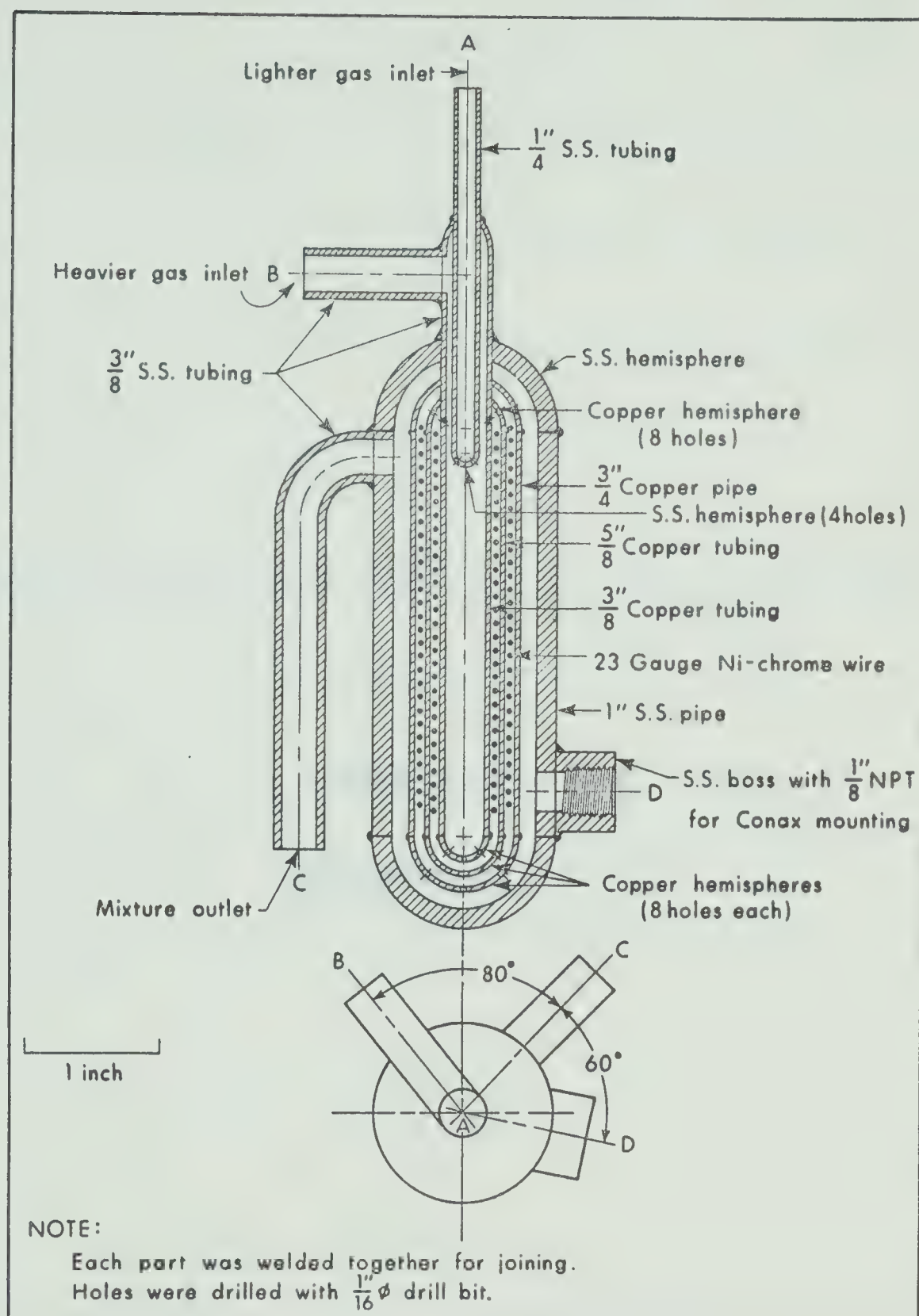


Figure 27. Drawing for the Excess Enthalpy Mixing Chamber

APPENDIX B

CALIBRATIONS

Table VIII

Calibration Data for 7555-1-B Type K-5 Potentiometer

(Serial No. 1745006)

1.6	Volts range $\pm(0.001\% + 2 \mu\text{V})$
0.16	Volt range $\pm(0.001\% + 0.2 \mu\text{V})$
0.016	Volt range $\pm(0.003\% + 0.1 \mu\text{V})$

Table IX

Calibration Data for 8163-B Platinum Resistance Thermometer

(Serial No. 1720571)

The following values were found for the constants in the equation:

$$t = \frac{R_t - R_0}{\alpha R_0} + \delta \left(\frac{t}{100} - 1 \right) + \beta \left(\frac{t}{100} - 1 \right) \left(\frac{t}{100} \right)^3 \quad (70)$$

in which t is the temperature, at the outside surface of the tube protecting the platinum resistor, in $^{\circ}\text{C}$ on the International Practical Temperature Scale of 1948 and R_t and R_0 are the resistances of the platinum resistor at t° and 0°C , respectively, measured with a continuous current of 2.0 milliamperes and a minimum immersion of 7 inches.

$$R_0 = 25.564 \text{ absolute ohms}$$

$$\alpha = 0.00392625$$

$$\delta = 1.4924$$

$$\beta = 0.1092 \text{ (t below } 0^{\circ}\text{C)}$$

$$0 \quad \text{(t above } 0^{\circ}\text{C)}$$

The values given are determined from measurements at the triple point of water, tin point, zinc point and the oxygen point.

The error introduced by using linear interpolation from the data computed above equation will be less than 0.0001°C .

Table X

Calibration Data for 4015-B Standard Resistor

(Serial No. 1740278)

The four-terminal resistance value, using the two top thumbscrews as potential terminals, and either the two side thumbscrews or the amalgamated surfaces as current terminals, was

0.09997 ohm.

The two-terminal value, that is the resistance between the amalgamated surfaces of the terminals, was

0.10002 ohm.

Resistance Uncertainty: 0.03%

Resistor Rating: 1 watt

Table XI

Calibration Data for 4025-B Standard Resistor

(Serial No. 1737342)

The four-terminal resistance value of the above designated standard resistor at 25°C, was

9.99995 ohms.

Resistance Uncertainty: 0.001%

Within the interval 20° to 35°C, the change of resistance with temperature for a manganin resistor is accurately expressed by the equation

$$R_T = R_{25} [1 + \alpha (T - 25) + \beta (T - 25)^2] \quad (71)$$

where R_T is the resistance at $T^\circ\text{C}$, R_{25} is the resistance at 25°C, and α and β are constants. Experience shows that the coefficients α and β do not change appreciably with time and hence need to be determined only once.

$$\alpha = + 0.000001$$

$$\beta = - 0.0000005$$

Table XII

Calibration of Moseley 7100B Strip Chart Recorder

(Serial No. 819-02586)

<u>Channel 1</u>		<u>Channel 2</u>	
<u>Actual (mV)</u>	<u>Recording</u>	<u>Actual (V)</u>	<u>Recording</u>
0	0	0	0
10	10.0	1	1.003
20	20.0	2	2.006
30	30.0	3	2.990
40	40.0	4	3.995
50	50.0	5	5.00
60	60.0	6	6.01
70	70.01	7	7.01
80	80.02	8	8.02
90	90.02	9	9.03
100	100.0	10	10.02
110	109.6	11	11.02
120	119.8	12	12.02
130	129.8	13	13.02
140	139.8	14	14.02
150	150.2	15	15.04
160	160.1	16	16.04
170	170.0	17	17.04
180	180.0	18	18.06
190	190.2	19	19.08
200	199.0	20	20.06
210	210.0	21	21.02
220	220.5	22	22.05
230	231.0	23	23.05
240	240.5	24	24.05
250	250.2	25	25.05
260	260.0	26	26.05
270	270.0	27	27.05
280	280.5	28	28.05
290	290.5	29	29.05
300	300.0	30	30.00
310	310.5	31	31.05
320	321.0	32	32.05
330	331.0	33	33.0
340	341.2	34	34.05
350	351.5	35	35.05
360	361.7	36	36.05
370	371.7	37	37.05
380	381.5	38	38.10
390	392.0	39	39.1
400	402.0	40	40.1

Table XIII

Gasometer Calibration

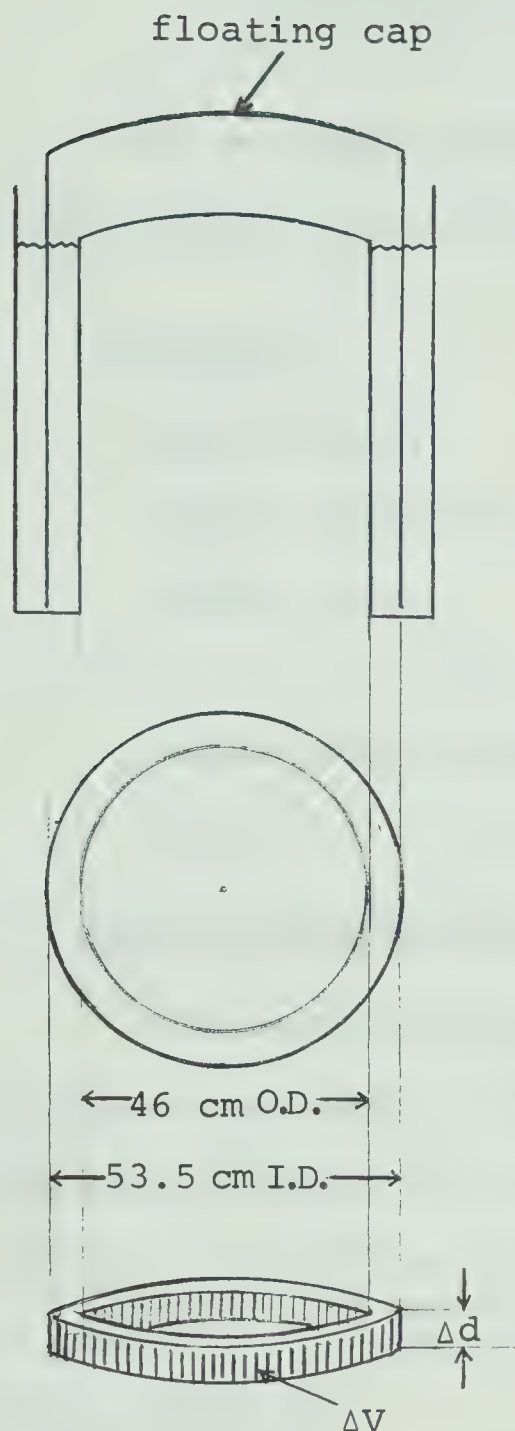
Water temperature: 18°C

Density of water at 18°C: 0.9986 gm/cc

Sensitivity of balance: ±0.1 lb.

The zero point of the height of water level was taken at the circumference 2 cm below from the lid of hemisphere part of the gasometer.

<u>Total Weight</u> <u>(lbs.)</u>	<u>Height of Water</u> <u>Level(cm)</u>		<u>Total Weight</u> <u>(lbs.)</u>	<u>Height of Water</u> <u>Level(cm)</u>	
	<u>Up</u>	<u>Down</u>		<u>Up</u>	<u>Down</u>
15	-	-3.1	210	36.9	37.1
20	-	-2.1	220	38.9	39.1
25	-	-1.1	230	40.9	41.1
30	-	0	240	43.0	43.2
35	-	+1.1	250	45.0	45.2
40	-	2.1	260	47.1	47.3
50	-	4.1	270	49.1	49.3
60	6.0	6.1	280	51.2	51.4
70	8.0	8.2	290	53.2	53.4
80	10.0	10.1	300	55.3	55.5
90	12.0	12.2	310	57.2	57.4
100	14.2	14.5	320	59.3	59.5
110	16.4	16.6	325	60.4	-
120	18.5	18.6	330	61.4	61.6
130	20.4	20.6	340	63.4	63.6
140	22.5	22.6	350	65.5	65.6
150	24.7	24.6	360	67.5	67.6
160	26.8	26.8	370	69.5	69.7
170	28.8	28.9	380	70.6	71.8
180	30.9	31.0	390	73.6	73.8
190	32.9	33.0	395	74.6	74.6
200	35.0	35.1			



Correction for the gasometer

floating cap thickness

$$\begin{aligned}\Delta V &= \frac{\pi}{4} (\text{I.D.}^2 - \text{O.D.}^2) \cdot \Delta d \\ &= \frac{\pi}{4} (53.5^2 - 46^2) \cdot \Delta d \\ &= 580 \cdot \Delta d\end{aligned}$$

If $\Delta d = 1 \text{ cm}$, $\Delta V = 580 \text{ cc/cm}$

Water level changed in 9 mm when gasometer floating distance was 65 cm.

$$\begin{aligned}\therefore \Delta \bar{V} &= \frac{9 \text{ mm}}{65 \text{ cm}} \times \frac{580 \text{ cc}}{1 \text{ cm}} \times \frac{1 \text{ cm}}{10 \text{ mm}} \\ &= 8.03 \text{ cc/cm}\end{aligned}$$

Correlation between volume and floating distance

Choosing the starting point at 6.1 cm and the end point at 69.7 cm from the calibration table, then:

$$\begin{aligned}\bar{V} &= \frac{(370-60) \text{ lb}}{(69.7-6.1) \text{ cm}} \times \frac{1 \text{ cc}}{0.9986 \text{ gm}} \times \frac{453.6 \text{ gm}}{1 \text{ lb}} \\ &\approx 2,214 \text{ cc/cm}\end{aligned}$$

$$\begin{aligned}\therefore V &= 2,214 + 8.03 \\ &= 2,222 \text{ cc/cm}\end{aligned}$$

Table XIV

Calibration of Gas Chromatograph

To analyze nitrogen-carbon dioxide mixture a gas chromatograph was installed and calibrated as follows.

1. Conditions

Carrier gas:	Helium
Carrier gas flow rate:	68.9 cc/min
Column used:	60-100 mesh silica gel in 13 inches in the $\frac{1}{4}$ inch I.D. glass tube.
Column temperature:	107°F
Sample gas flow rate:	0.06 S.C.F.H.

2. Standard Mixture Preparation

The weighing method⁴³ was used. That is, using an evacuated cylinder of known weight, standard mixtures are prepared by adding and weighing each gas. The weight of each gas is found by difference, and the number of moles is computed. The mole fraction is computed from the total number of moles.

3. Calibration Data

A total of 11 samples were used to calibrate the gas chromatograph. The actual data points are as follows:

Area Ratio ($\frac{\text{Area N}_2}{\text{Total Area}}$)	Mole Fraction N ₂ (calculated from weights)
0.1013	0.11657
0.2436	0.27047
0.2795	0.31132
0.3210	0.35113
0.4105	0.44431
0.5121	0.54214
0.6116	0.64155
0.6373	0.66993
0.6725	0.70162
0.7220	0.75290
0.8030	0.82306

From the data above the following equation is established.

$$y = 0.14034 x^2 + 0.85966 x \quad (72)$$

where x is mole fraction of nitrogen, and y is the area ratio.

Equation (72) reproduces the experimental calibration data within $\pm 0.86\%$.

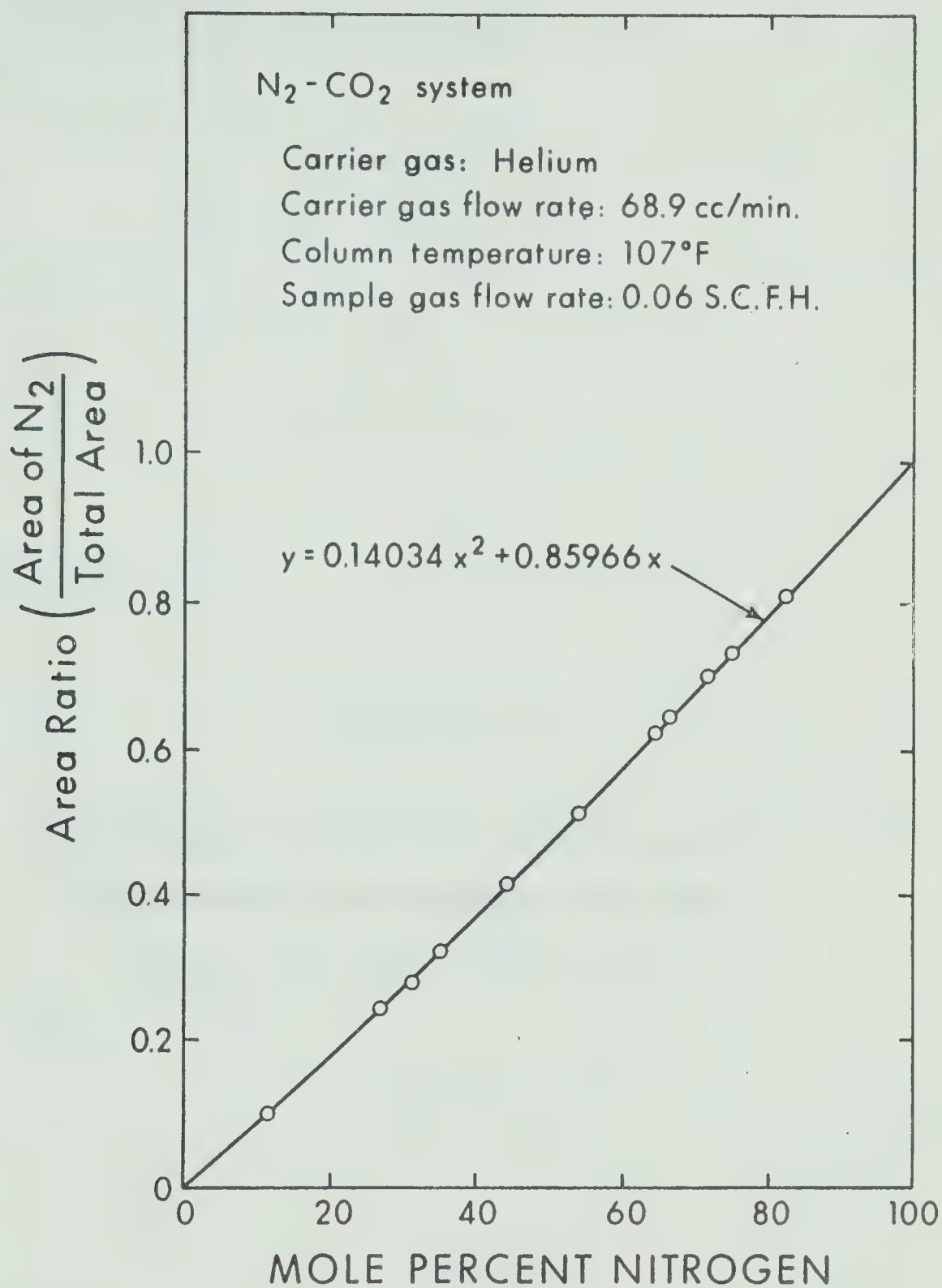


Figure 28. Calibration of the Gas Chromatograph for Analysis of Nitrogen-Carbon Dioxide Mixtures

APPENDIX C

B-W-R ENTHALPY DEPARTURE FORMULA USED IN
CALCULATION, ITS CONSTANTS USED AND
COMBINATION RULES FOR MIXTURE

(1) Enthalpy Departure Equation

$$\begin{aligned}
H - H^{\circ} = & (B_{\circ}RT - 2A_{\circ} - 4C_{\circ}T^{-2}) V^{-1} \\
& + \frac{1}{2} (2bRT - 3a)V^{-2} + \frac{6}{5} a_{\alpha}V^{-5} \\
& + cV^{-2} T^{-2} \{3[(1 - e^{-\gamma V^{-2}})/\gamma V^{-2}] \\
& - (\frac{1}{2} - \gamma V^{-2})e^{-\gamma V^{-2}}\}
\end{aligned}
\tag{73}$$

(2) Constants Used

Table XV

Constants Used for the B-W-R Equation of StateUnits: atmospheres, liters, gram-moles, $^{\circ}\text{K}$ $R = 0.08206$ $T(^{\circ}\text{K}) = 273.15 + T(^{\circ}\text{C})$

	<u>Carbon Dioxide</u>	<u>Nitrogen</u>	
	<u>Cullen & Kobe</u> ¹⁴	<u>Bloomer & Rao</u> ⁶	<u>Crain & Sonntag</u> ¹³
A_{\circ}	2.73742	1.053642	0.872086
B_{\circ}	0.0499101	0.0407426	0.0281066
C_{\circ}	138567.	8059.	7813.75
a	0.136814	0.025102	0.0312319
b	0.0041239	0.0023277	0.0032351
c	14918.	728.41	547.364
α	0.000087	0.00012720	0.0000709232
γ	0.005394	0.0053	0.0045

(3) Combination Rules

Table XVI

Combination Rules Used for the B-W-R Equation of State

$$\begin{aligned}
A_{om} &= \left(\sum_i x_i A_{oi}^{1/2} \right)^2 \\
B_{om} &= \sum_i x_i B_{oi} \\
C_{om} &= \left(\sum_i x_i C_{oi}^{1/2} \right)^2 \\
a_m &= \left(\sum_i x_i a_i^{1/3} \right)^3 \\
b_m &= \left(\sum_i x_i b_i^{1/3} \right)^3 \\
c_m &= \left(\sum_i x_i c_i^{1/3} \right)^3 \\
\alpha_m &= \left(\sum_i x_i \alpha_i^{1/3} \right)^3 \\
\gamma_m &= \left(\sum_i x_i \gamma_i^{1/2} \right)^2
\end{aligned}$$

APPENDIX D

EXPERIMENTAL RAW DATA

Table XVIII

Experimental Raw Data of the Nitrogen-Carbon Dioxide System

1. 1-2 combination											
Room temperature: 21°C Barometric pressure: 708 mm Hg											
P (atm)	Time (min)	E ₁ (Volt)	E ₂ (mV)	F ($\mu\text{m/s}$)	H ^F (J/N)	P (atm)	M.F. N ₂	Area ratio	P (atm)	M.F. N ₂	Area ratio
17.5	5.33	25.00	131.41	0.01760	1918.79	128.1	0.1139	0.3036	127.5	0.1139	0.3036
17.4	5.42	25.00	126.20	0.01675	1833.09	126.1	0.1097	0.0960	124.9	0.1097	0.0960
17.4	3.39	32.50	164.79	0.02325	2032.09	123.4	0.1030	0.1030	123.7	0.1030	0.1030
17.3	3.49	31.50	165.10	0.02325	2168.55	122.3	0.0874	0.1000	122.2	0.0874	0.1000
17.2	3.62	30.80	155.92	0.02488	1921.85	123.6	0.0889	0.1017	121.1	0.0889	0.1017
17.2	3.52	30.00	152.27	0.02493	1822.11	118.3	0.0714	0.0819	120.3	0.0714	0.0819
17.6	3.67	29.00	145.54	0.02464	1724.09	116.2	0.0762	0.0873	118.8	0.0762	0.0873
17.5	3.33	30.50	154.07	0.02716	1735.62	114.5	0.0639	0.0791	117.0	0.0639	0.0791
17.0	3.31	30.75	155.92	0.02732	1754.42	113.8	0.0645	0.0741	116.2	0.0645	0.0741
17.1	3.29	31.25	152.53	0.02743	1801.81	112.1	0.0646	0.0742	115.2	0.0646	0.0742
17.3	3.35	31.25	153.59	0.02716	1823.72	111.1	0.0647	0.0743	114.2	0.0647	0.0743
17.7	3.31	31.50	159.57	0.02732	1839.29	110.1	0.0608	0.0699	113.2	0.0608	0.0699
17.7	3.28	32.50	162.43	0.02757	1885.43	108.7	0.0671	0.0679	111.8	0.0671	0.0679
17.5	3.23	32.50	164.79	0.02749	1947.85	107.4	0.0584	0.0671	110.7	0.0584	0.0671
17.5	3.27	33.00	167.45	0.02766	1936.30	106.4	0.0574	0.0674	108.7	0.0574	0.0674
17.5	3.22	34.20	173.45	0.02809	2111.52	105.0	0.0592	0.0681	107.5	0.0592	0.0681
17.4	3.22	34.50	175.22	0.02809	2151.081	103.6	0.0615	0.0707	106.2	0.0615	0.0707
17.2	3.35	34.50	175.22	0.02800	2238.09	101.9	0.0625	0.0718	105.3	0.0625	0.0718
17.3	3.34	35.50	181.64	0.02753	2367.79	100.2	0.0633	0.0727	104.3	0.0633	0.0727
17.4	3.34	36.00	182.93	0.02758	2430.25	98.9	0.0673	0.0773	103.3	0.0673	0.0773
17.6	3.32	36.50	185.55	0.02724	2436.97	96.8	0.0685	0.0786	101.8	0.0685	0.0786
17.2	3.32	37.00	187.74	0.02724	2549.37	95.5	0.0710	0.0815	99.9	0.0710	0.0815
17.8	3.32	37.50	190.34	0.02724	2619.71	94.1	0.0768	0.0880	97.3	0.0768	0.0880
17.3	3.32	38.00	192.22	0.02724	2681.22	92.8	0.0813	0.0931	95.7	0.0813	0.0931
17.8	3.31	37.50	190.34	0.02732	2611.82	90.7	0.0850	0.0973	94.0	0.0850	0.0973
17.4	3.25	36.50	185.65	0.02783	2434.54	88.3	0.0874	0.1000	92.1	0.0874	0.1000
17.0	3.28	35.50	179.91	0.02757	2315.86	87.0	0.0900	0.1029	90.4	0.0900	0.1029
17.7	3.28	34.50	172.30	0.02757	2124.14	85.3	0.1033	0.1178	87.0	0.1033	0.1178
17.3	3.26	35.50	184.79	0.02774	1930.09	79.8	0.1085	0.1237	85.5	0.1085	0.1237
17.6	3.30	35.00	182.27	0.02741	1966.51	76.4	0.1254	0.1425	82.0	0.1254	0.1425
17.4	3.25	29.00	146.85	0.02774	1594.75	73.7	0.1318	0.1496	75.7	0.1318	0.1496
17.2	3.26	27.50	139.55	0.02774	1383.01	71.0	0.1370	0.1554	73.0	0.1370	0.1554
17.2	3.23	25.00	127.33	0.02749	1155.05	63.3	0.1450	0.1642	64.7	0.1450	0.1642
17.4	3.27	22.50	113.58	0.02766	924.65	65.2	0.1589	0.1795	59.8	0.1589	0.1795
17.1	3.27	23.00	101.79	0.02766	735.35	61.1	0.1660	0.1873	52.5	0.1660	0.1873
17.0	3.25	18.00	91.67	0.02783	592.87	57.4	0.1722	0.1941	48.7	0.1722	0.1941
17.5	3.25	17.50	89.63	0.02783	567.17	53.3	0.1830	0.2059	46.7	0.1830	0.2059
17.1	3.25	16.00	81.55	0.02732	467.64	43.6	0.1938	0.2242	43.2	0.1938	0.2242
17.5	3.26	15.00	76.34	0.02774	412.70	45.0	0.2122	0.2376	42.3	0.2122	0.2376
17.4	3.26	14.00	71.13	0.02774	358.88	40.4	0.2154	0.2410	38.3	0.2154	0.2410
17.0	3.24	13.00	65.02	0.02732	307.40	35.8	0.2262	0.2527	33.0	0.2262	0.2527
17.0	3.23	12.00	60.91	0.02800	260.98	30.0	0.2322	0.2591	28.3	0.2322	0.2591
17.4	3.23	11.00	55.50	0.02930	219.38	23.4	0.2632	0.2930	23.0	0.2632	0.2930
17.0	3.22	10.00	51.00	0.02803	181.54	20.3	0.2535	0.2819	20.3	0.2535	0.2819
17.0	3.22	9.00	45.89	0.02809	147.01	16.6	0.2655	0.2946	16.6	0.2655	0.2946
17.0	3.22	8.00	40.67	0.02809	115.83	12.8	0.2655	0.2946	12.8	0.2655	0.2946
17.0	4.28	5.90	30.03	0.02113	83.85	11.0	0.2940	0.3247	11.0	0.2940	0.3247
17.9	4.26	5.50	27.95	0.02123	72.39	7.7	0.2765	0.3063	7.7	0.2765	0.3063
17.6	4.26	5.00	25.24	0.02123	59.43	6.0	0.2735	0.3031	6.0	0.2735	0.3031
17.5	6.26	4.00	20.12	0.01445	55.72	4.3	0.2720	0.3015	4.3	0.2720	0.3015
17.5	6.26	3.70	18.77	0.01445	46.06						
17.4	6.25	3.20	16.16	0.01447	35.74						
17.9	6.25	3.00	15.12	0.01447	31.34						

* The number and type of nitrogen cylinders used with one 50 lbs. carbon dioxide cylinder.

5. 4 K combination

Room temperature: 19.9°C
Barometric pressure: 704.0 mm Hg

P (atm)	Time (min)	E ₁ (Volt)	E ₂ (mV)	F (r-s/s)	H ² (J/M)	P (atm)	Area Ratio	M.P. N ₂
133.9	3.91	35.00	176.35	0.02309	2703.30	130.5	0.5220	0.5565
130.5	3.91	34.50	175.22	0.02309	2617.93	130.0	0.5440	0.5732
130.0	3.97	33.50	173.32	0.02274	2503.55	129.2	0.5595	0.5033
128.3	3.98	32.75	166.88	0.02268	2499.17	128.5	0.5650	0.5937
127.5	3.99	32.75	166.88	0.02315	2360.75	127.8	0.5605	0.5943
125.8	3.94	33.00	167.92	0.02291	2416.19	126.8	0.5625	0.5962
126.1	3.70	34.00	173.13	0.02440	2412.36	126.1	0.5500	0.5240
125.1	3.72	34.00	173.13	0.02427	2425.40	125.1	0.5430	0.5821
124.4	3.75	34.50	175.22	0.02437	2510.81	124.5	0.5390	0.5733
123.9	3.76	34.50	175.22	0.02401	2517.50	123.7	0.5280	0.5625
122.9	3.73	34.75	176.78	0.02332	2571.50	122.7	0.5270	0.5576
121.3	3.35	35.00	177.93	0.02345	2654.04	122.0	0.5060	0.5438
119.8	3.66	36.00	183.56	0.02466	2678.36	121.3	0.5060	0.5468
117.2	3.76	36.50	185.65	0.02431	2621.75	120.3	0.5120	0.5467
115.9	3.73	36.75	187.21	0.02383	2910.50	119.3	0.4940	0.5289
114.7	3.63	36.75	187.21	0.02357	2918.50	117.6	0.4970	0.5319
112.8	3.62	36.50	193.47	0.02474	2947.75	117.2	0.4660	0.5210
111.3	3.65	38.10	194.20	0.02473	2931.24	115.5	0.4650	0.5210
110.9	3.68	38.10	194.20	0.02453	3015.83	114.9	0.4470	0.4820
107.7	3.78	38.00	193.47	0.02358	3077.53	112.3	0.4370	0.4719
103.6	3.51	39.00	195.37	0.02572	3007.71	106.9	0.4210	0.4538
103.0	3.73	37.60	191.91	0.02470	2981.04	103.2	0.4250	0.4598
102.1	3.77	37.50	193.16	0.02394	2982.67	102.5	0.4420	0.4770
101.9	3.77	37.60	193.16	0.02394	2988.53	101.9	0.4460	0.4810
100.3	3.50	38.50	196.78	0.02579	2926.45	101.3	0.4570	0.4920
99.4	3.46	38.75	197.33	0.02509	2930.37	100.2	0.4560	0.4910
98.0	3.52	38.50	193.17	0.02564	2864.77	99.1	0.4500	0.4850
96.2	3.46	37.50	190.86	0.02609	2742.91	98.6	0.4630	0.4950
95.6	3.46	37.60	188.26	0.02639	2669.37	96.8	0.4420	0.4770
94.9	3.49	36.50	185.65	0.02537	2619.34	96.2	0.4780	0.5130
94.3	3.04	38.50	196.78	0.02569	2541.83	95.5	0.4830	0.5150
92.6	3.03	38.00	193.37	0.03009	2441.56	94.5	0.5050	0.5398
91.0	2.65	39.00	193.58	0.03407	2273.17	93.8	0.4960	0.5309
89.6	2.50	38.50	196.08	0.03611	2070.32	93.3	0.5050	0.5398
87.1	2.12	38.50	196.08	0.04238	1772.59	90.7	0.5130	0.5477
84.8	1.75	38.50	196.08	0.03159	1463.22	87.3	0.5430	0.5772
82.9	1.59	37.50	190.86	0.05678	1263.47	84.3	0.5700	0.6035
81.7	1.57	35.50	185.65	0.05750	1178.33	82.2	0.5780	0.6113
80.1	1.54	35.00	177.93	0.05662	1062.23	81.1	0.5850	0.6181
78.5	1.37	33.50	167.92	0.05750	963.59	79.6	0.5950	0.6277
74.0	1.10	35.50	177.93	0.08207	738.29	78.1	0.6030	0.6355
70.6	0.92	35.00	177.93	0.09213	634.21	73.4	0.6350	0.6562
67.9	0.35	32.50	162.70	0.09563	547.83	70.0	0.6540	0.6843
61.7	0.87	29.00	147.27	0.10377	411.53	66.0	0.6470	0.6776
59.4	0.50	27.60	137.56	0.10031	369.69	64.5	0.6760	0.7051
56.9	0.94	25.00	127.14	0.09605	330.92	61.1	0.6820	0.7108
53.5	0.99	22.50	114.62	0.09119	232.79	58.1	0.7060	0.7334
48.5	1.03	20.00	102.00	0.09028	225.95	56.0	0.7090	0.7362
44.0	1.01	18.00	91.78	0.08939	184.81	52.3	0.7260	0.7521
39.0	1.01	16.50	81.35	0.08939	145.60	47.9	0.7370	0.7624
33.2	1.01	14.00	71.13	0.08939	111.40	45.1	0.7500	0.7745
27.1	1.20	12.00	60.91	0.09028	80.95	40.7	0.7550	0.7791
20.8	1.00	10.00	51.00	0.09028	56.48	37.7	0.7650	0.7934
19.1	2.29	6.00	30.65	0.03942	46.34	35.6	0.7740	0.7967
13.6	2.79	5.00	25.24	0.03942	32.00	30.2	0.7850	0.8068
9.1	2.59	4.00	20.23	0.03942	20.52	25.7	0.7860	0.8077
6.8	2.29	3.50	17.73	0.03942	15.74	22.7	0.7820	0.8041
						18.3	0.8030	0.8206
						13.2	0.8030	0.8234
						11.1	0.8080	0.8279
						9.4	0.8200	0.8389
						7.0	0.8280	0.8462

APPENDIX E

SAMPLE CALCULATION

1. Bath Temperature

In Equation (31)

$$E_p = 54.1862 \text{ mV}$$

$$E_s = 19.6426 \text{ mV}$$

$$R_p = 25.564 \text{ ohms}$$

and R_s is obtained from Equation (71) at 22°C as:

$$R_s = 9.999874 \text{ ohms}$$

$$\begin{aligned} \therefore Y &= \frac{(54.1862)(9.999874)}{(19.6426)(25.564)} \\ &= 1.079084 \end{aligned}$$

From conversion table

Temperature Deg. C	Resistance Ratio	Inverse Difference
19	1.075501	252.324
20	1.079463	252.398

$$\begin{aligned} \therefore T_{\text{bath}} &= 20 - (1.079463 - 1.079084) \times 252.398 \\ &= 19.9043^\circ\text{C} \end{aligned}$$

2. Flow Rate

In Equation (32)

$$V_m = 2,222 \text{ cc/cm}$$

$$d = 63.1 \text{ cm}$$

$$P_m = 705 \text{ mm Hg}$$

$$T_m = 21.0^{\circ}\text{C}$$

$$z_m = 0.9988$$

$$\theta = 1.13 \text{ min or } 67.8 \text{ sec}$$

$$\therefore F_m = 0.0795 \text{ gram-mole/sec}$$

3. Power Supply

In Equation (37)

$$E_1 = 12.0 \text{ V}$$

$$E_2 = 61.3 \text{ mV}$$

$$\therefore \dot{W} = 7.356 \text{ watts or } 7.356 \text{ Joules/sec}$$

4. Excess Enthalpy

In Equation (38)

$$\dot{W} = 7.356 \text{ Joules/sec}$$

$$F_m = 0.0795 \text{ gram-mole/sec}$$

$$\therefore H^E = \frac{7.356}{0.0795} = 92.5 \text{ Joules/gm-mole}$$

Note:

This result is listed in the eighth line for the temperature of $19.93 \pm 0.05^{\circ}\text{C}$, nominal 26 mole percent nitrogen in Table XVII, Appendix D.

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